

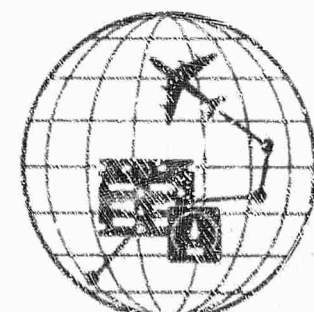
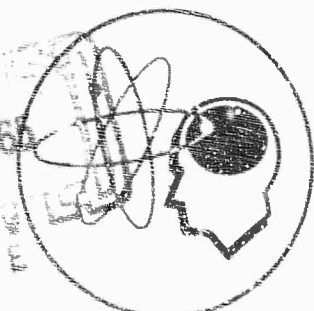
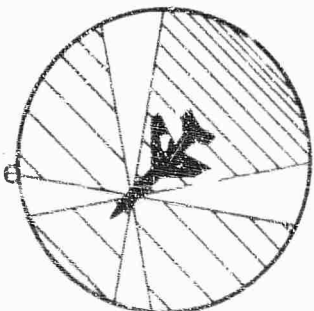
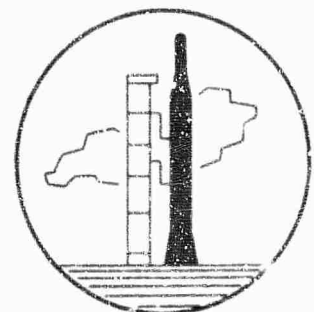
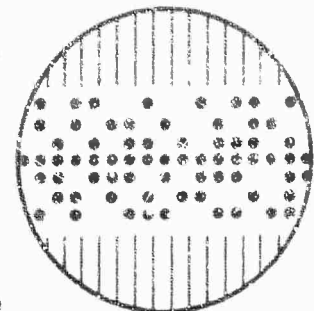
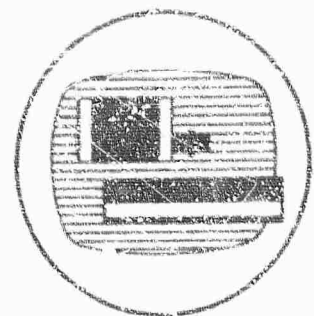
PUMPED TRANSFORMER LASERS

TECHNICAL SUMMARY REPORT NO. 2, FOR THE
PERIOD 1 MAY 1965 to 1 NOVEMBER 1965

Contract Nonr-4718(00), ARPA No. 306
GPL Division, Aerospace Group, General Precision, Inc.

Cecil B. Ellis (Sections 1 - 9)
James H. Simpson and Donald S. Bayley (Section 10)
Donald S. Bayley (Section 11)

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GPL A-31-2

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ABSTRACT

Most of the analysis in this period has dealt with use of metastable nitrogen molecules as the active medium for a transformer laser to be pumped by a battery of Nd glass auxiliary lasers. It was concluded that such a medium would be operable, but that adequate data are not at hand to produce optimism on reaching maximum output pulse energy densities in the nitrogen greater than the region of one joule/cm³, with satisfactory maintenance of optical beam quality.

An extension of previous analysis on a similar use of CN molecules indicates that this medium might be expected to yield satisfactory outputs around one joule/cm³ or somewhat greater.

From the meager information available today, it appears that diatomic cesium molecules might possibly surpass CN and constitute the best medium for transformer action with Nd glass laser pumping.

An experimental attack on some of the many remaining unknowns regarding Cs₂ is now underway, and first preliminary tests are reported.

A beginning has been made toward mathematical spatial analysis of the high power flux patterns to be expected within a heavily pumped transformer medium.

TABLE OF CONTENTS

	<u>Page No.</u>
1. INTRODUCTION	1
2. THE LOWER ELECTRONIC STATES AND OPTICAL TRANSITIONS OF N_2	3
2.1 Electronic States and Selection Rules	3
2.2 Potential Curves and the Transitions near 1.06μ	6
2.3 Possible Pumping and Lasing Bands	10
3. STRUCTURE OF THE NITROGEN FIRST POSITIVE BANDS	16
3.1 Rotational Levels of $N_2 \cdot A(v = 0)$	16
3.2 Rotational Levels of $N_2 \cdot B(v = 0)$	17
3.3 Rotational Branches of the $N_2 \cdot (B-A)$ Bands	21
4. LASING POSSIBILITIES IN THE (0, 0) BAND AT 80°K	26
4.1 80° K Boltzmann Rotational Distributions for $(v = 0)$ in $N_2 \cdot A$ and $N_2 \cdot B$	26
4.2 Equilibrium Excitation for Zero-Gain at Each (0, 0) Line Wavelength	31
5. EXCITED-STATE POPULATION LIMITS ON NITROGEN TRANSFORMER POWER	38
5.1 Population Needed for a Desired Power Density	38
5.2 Fluorescence Losses from the $N_2 \cdot A$ State	40
5.3 Impurity Quenching of $N_2 \cdot A$	40
5.4 Electronic-to-Vibrational Quenching of $N_2 \cdot A$	42
5.5 Metastable-Metastable Quenching of $N_2 \cdot A$	44
5.6 Losses from $N_2 \cdot B$	48

TABLE OF CONTENTS (continued)

	<u>Page No.</u>
6. CONCLUSIONS ON NITROGEN AS A MEDIUM WITH Nd PUMPING	51
7. MONOMER POPULATION LIMITS ON CYANOGEN TRANSFORMER POWER	52
7.1 Population Needed for a Desired Power Density	52
7.2 Types of Collision Processes Possible in the Cyanogen Medium	54
7.3 Three-Body Recombination of CN in Helium	58
8. CONCLUSIONS ON CYANOGEN AS A MEDIUM WITH Nd PUMPING	61
9. ADDITIONAL MEDIA CONSIDERED DURING THE REPORT PERIOD	62
9.1 The Se_2 Molecule	62
9.2 The I_2 Molecule	63
9.3 The CO Molecule and Others	64
9.4 The Cs_2 Molecule	65
10. EXPERIMENTS ON THE SPECTRUM OF Cs_2	66
11. SPATIAL FLUX ANALYSIS	69
ACKNOWLEDGEMENTS	75
BIBLIOGRAPHY	76

LIST OF FIGURES AND TABLES

<u>Figure</u>		<u>Page No.</u>
1.	The Lower Electronic States and Transitions of the N_2 Molecule	4
2.	Potential Curves and Vibration Levels of N_2	7
3.	N_d and N_2 Band Location Map	9
4.	Rotational Levels of the ($v = 0$) Level of $N_2 \cdot A$	18
5.	Rotational Levels of the ($v = 0$) Level of $N_2 \cdot B$	19
6.	Labelling System for the $N_2 \cdot (B-A)$ Branches	22
7.	Chart of the (1, 0) Band of $N_2 \cdot (B-A)$ at Low Temperature	25
8.	80° K Boltzmann Rotational Distribution for ($v = 0$) of $N_2 \cdot A$	28
9.	80° K Boltzmann Rotational Distribution for ($v = 0$) of $N_2 \cdot B$	30
10.	$\left[Z_0 \right]_{80}$ for the (0, 0) Band	34
11.	$\left[Z_0 \right]_{80}$ vs. Wavenumber, for the (0, 0) Band	37
12.	Absorption Spectrum of Cs_2 near 1μ	68
<u>Table</u>		
1.	Location of Nitrogen First Positive Band Heads	14
2.	Collision Processes in the Cyanogen Medium	56
3.	Equivalent Four-Level Cycle	69

1. INTRODUCTION

The first Technical Summary Report of this series, GPL Division's Report GPL A-31-1, dated 17 May 1965, with the same title as the present report, described the background of the work here continued and contained numerous details of the spectroscopic principles involved in the transformer laser concept being studied. This material will not be repeated; the discussion in this report will presume a knowledge of the presentation in GPL A-31-1.*

The transformer laser concept is an arrangement proposed for combining the outputs of numerous auxiliary lasers, which do not need to be in phase, and which do not need to be of the best optical quality, into a single coherent diffraction-limited beam containing a power close to the sum of the auxiliary laser output powers. This is to be done by absorption of the pumping laser beams by the molecules of a transformer gas medium, in such a manner that inversion occurs and the gas re-emits most of the absorbed energy as a single new laser beam.

GPL A-31-1 mentioned a number of possible combinations of types of auxiliary pumping lasers and transformer gas media; however, it was largely concerned with a study of CN monomer gas molecules pumped by a battery of Nd glass lasers, for re-emission of a coherent beam in the neighborhood of 1.06μ .

* That report now carries the Dept. of Defense document number AD-618896. It is available to the public through the Office of Technical Services of the U.S. Dept. of Commerce.

Much of the present report will deal with the possibility of using
 $N_2 \cdot A$ metastable nitrogen molecules as the transformer medium, for
pumping with a group of Nd glass lasers.

Then, following a comparison of the present state of information
on the use of CN and $N_2 \cdot A$, this report will briefly consider the use
of diatomic alkali molecules such as Cs_2 as transformer media, with the
same pumping arrangement.

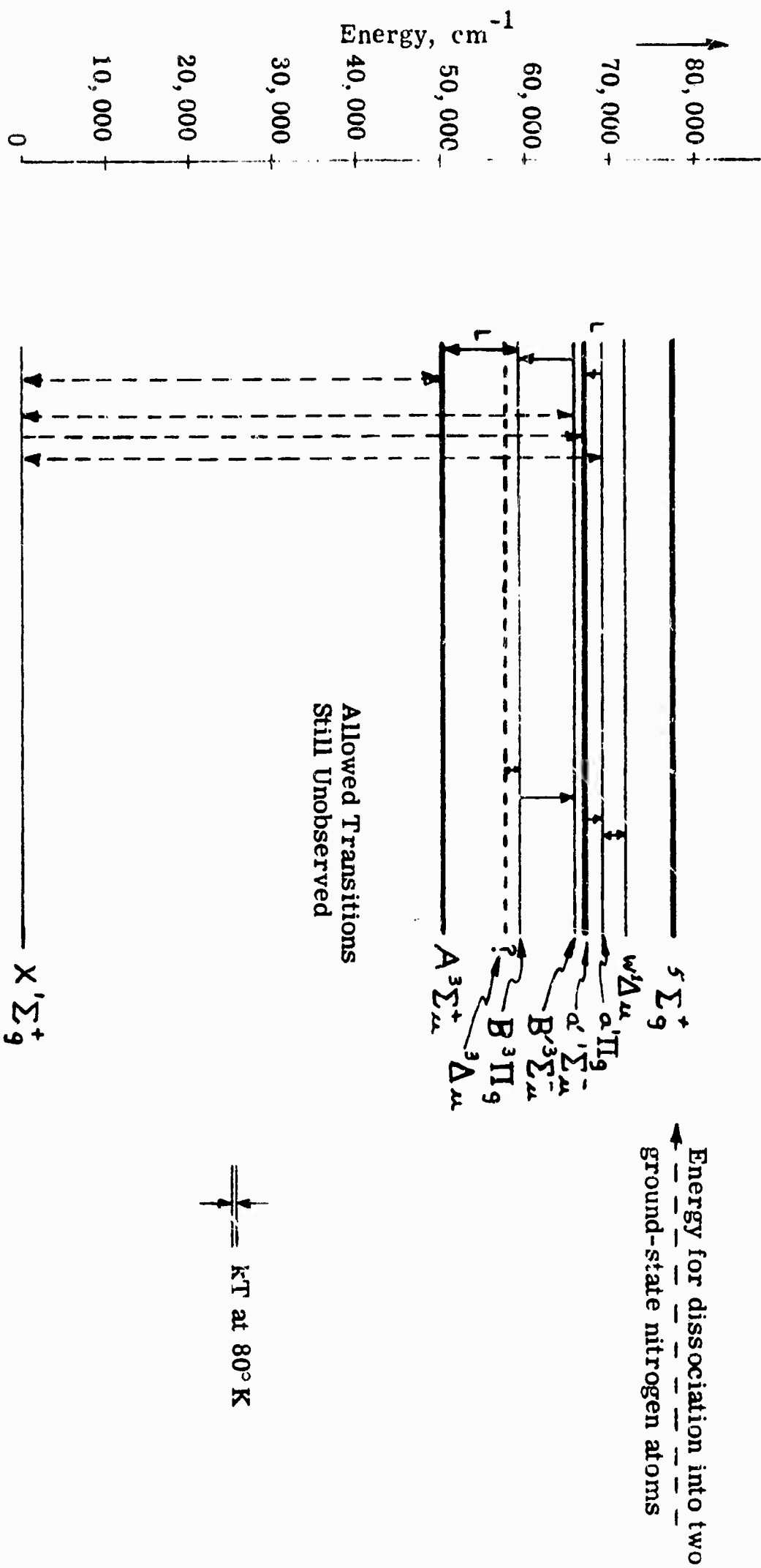


Figure 1. The lower electronic levels and transitions of the N_2 molecule. Lasers have already been operated on the transitions marked L. The lowest vibration states of the four levels shown with heavy lines are metastable. The $3\Delta_u$ level has not yet been definitely observed. The location shown is principally from theory. If $3\Delta_u$ should actually lie above B, its lowest vibrational states would not be metastable.

2. THE LOWER ELECTRONIC STATES AND OPTICAL TRANSITIONS OF N₂

2.1 Electronic States and Selection Rules

Figure 1 displays what are believed to be all of the electronic states of N₂ lying below the first dissociation limit of the molecule.

Both $^5\Sigma_g^+$ and $^3\Delta_u$ have been located only by inference; neither has yet been observed directly.* Theory indicates that probably no others remain undiscovered below 75,000 cm⁻¹, although numerous additional electronic states of the neutral nitrogen molecule lie at higher energies. The latest value for the first dissociation limit of N₂, from Tilford and Wilkinson (1964), is 78,737 cm⁻¹.

Unexcited nitrogen molecules will absorb in four ultraviolet band systems involving levels of this group. However, as shown in the diagram, these are all forbidden transitions, so the bands are rather weak. Several meter-atmospheres of N₂ are needed in the beam path for their detection. The (A - X) system constitutes the Vegard-Kaplan bands, and it lies principally in the region from 1500Å to around 3500Å, although some of its emission bands extend into the visible. Only the (6, 0) and (7, 0) bands near 1700Å, measured by Wilkinson (1959) at about 10m-atm path, have been seen in absorption so far. No (B - X) system has yet been observed; presumably it is extremely weak. Some of the (B' - X) system has been seen in absorption by Wilkinson (1962)

* Gilmore (1965) has most recently cumulated the existing information. The theoretical basis is chiefly by Mulliken (1957). The exact location of the $^3\Delta_u$ state is especially uncertain. However, it seems reasonable that whether it actually lies above or below state B, it is not separated from that state by more than perhaps 2000 cm⁻¹. (See the Bibliography for citations of all references indicated in this report by author's name and date.)

in the range $1500 - 1300\text{\AA}$. In emission it is more extended.

The $(a - X)$ and $a' - X$ systems have locations similar to $(B' - X)$.

All of these systems were observed first in emission from discharge tubes.

The $N_2 \cdot A$ state, as well as three others shown in the diagram, are radiatively metastable — at least in their lower vibrational and rotational levels. The spontaneous radiative lifetime of $N_2 \cdot A$ is believed to be at least 1 sec. Details on this point will be presented in a later section.

The very well known $N_2 \cdot (B \rightarrow A)$ bands are called, for historical reasons, the First Positive System of nitrogen. These bands are emitted rather strongly from many types of discharges, with the radiative lifetime of $N_2 \cdot B$ being about 10 microseconds. Whenever a large enough concentration of $N_2 \cdot A$ can be made, by some means, the 1st Pos. bands can be seen in absorption. This was first accomplished by Carleton and Oldenberg (1962) who created a steady-state population of about $10^{11} N_2 \cdot A$ molecules/cm³ in a discharge tube. At appreciable $N_2 \cdot A$ population densities, some of the 1st Pos. bands could absorb Nd glass laser light near 1.06μ , as will be shown in the next section.

Two other allowed transitions indicated on the diagram have been observed only in emission, since conditions have not yet been found for building up large concentrations in the lower levels.

As shown at the right in Figure 1, the electronic selection rules allow several other transitions which have not as yet been seen. Potentially, the most important of these for a laser transformer could be the $(B' - B)$ system in absorption. If primary preparation of $N_2 \cdot A$ molecules followed by Nd glass laser pumping in $(B \rightarrow A)$ should produce a heavy population of $N_2 \cdot B$, these molecules might then absorb a second Nd laser light quantum, and be excited to $N_2 \cdot B'$ — thus being at least temporarily removed from any $(B \rightarrow A)$ pump-lase cycle. However, the $(B' - B)$ bonds are rather weak when observed in emission with usual methods of excitation.

2.2 Potential Curves and the Transitions near 1.06μ

Figure 2 gives the most recent information on the potential energy curves and a few of the known vibrational levels of these low lying electronic states of nitrogen, as surveyed by Gilmore (1965).

It is apparent from the Franck-Condon principle why unexcited nitrogen gas at room temperature or below absorbs from the $(A - X)$ system only the $(6, 0)$ and $(7, 0)$ bands with appreciable intensity — together with probably a few others of the same sequence at still shorter wavelengths, not yet investigated. This arises from the considerable difference in average internuclear separation between the A state and the X state. Since the vibrational spacing in $N_2 \cdot X$ is over 2000 cm^{-1} , practically all the ground state molecules will be in $(v = 0)$ at these temperatures.

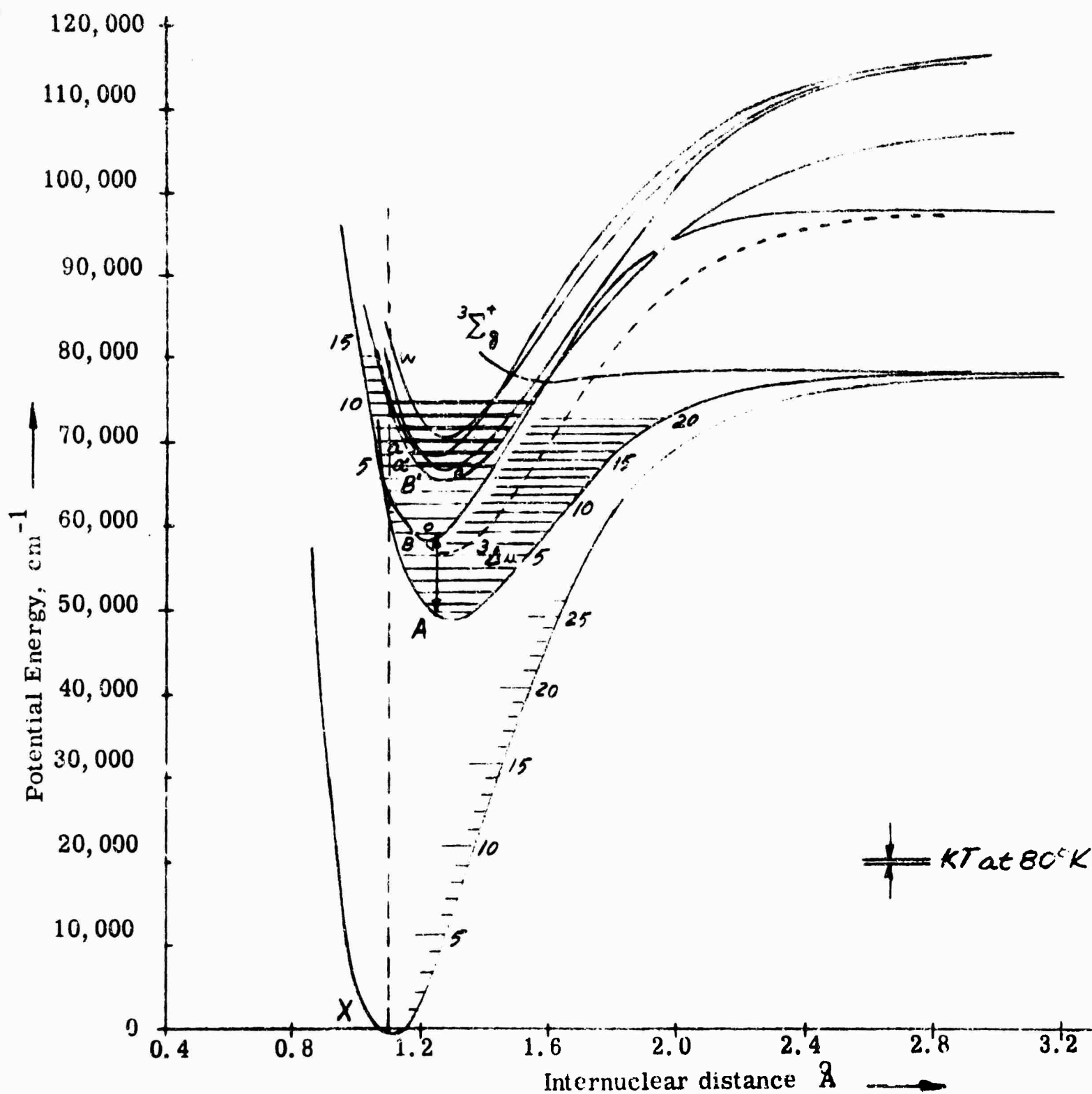


Figure 2. The lower electronic and vibrational states of N_2 , with their potential energy curves. (Data from Gilmore (1965)). The $3\Delta_u$ curve is largely a guess, as the state has not yet been observed. The $5\Sigma_g^+$ is principally theoretical. Probably only its ($v = 0$) level is stable. The vibrational spacing in the three upper singlet states is similar to that shown for the triplets.

Let us now ask which bands of the (B - A) system fall within the possible wavelength range of Nd laser light emission. Table 1 gives the locations of the P_1 heads of all bands involving the first 12 upper and lower vibration states* as either measured or calculated by Dieke and Heath (1959). The band head terminology and rotational structure will be discussed in a following section. It will be shown there that the most intense part of each band extends about 100 cm^{-1} toward increasing wavenumbers from the P_1 head. Figure 3 displays such approximate locations, as well as the relative intensities quoted by Dieke and Heath for emission spectra with conventional discharge tube excitation, for all of these bands falling within the Nd glass fluorescence region, in the manner of Figure 11 in Report GPL A-31-1.

In order to indicate possible effects from absorption of a second Nd light quantum in the ($B' - B$) transition, the more intense bands of this system expected to fall within the Nd emission region are also plotted in Figure 3. The molecular constants of the B' state have been determined with high precision by Tilford, Vanderslice, and Wilkinson (1965), and those of the B state with similar precision by Dieke and Heath (1959). The detailed structures of these ($B' - B$) bands have not been computed in the present contract work, but the band origins were located quite simply by subtraction between the two sets of first 12 vibrational levels. The band origins will lie

* Nitrogen molecules placed in ($v = 13$) or slightly higher vibrational levels of N_2 , B, or in very high rotation levels of ($v = 12$), are known to have a rather strong tendency toward dissociation of the molecule upon subsequent collisions. Dieke and Heath summarize the evidence on this matter.

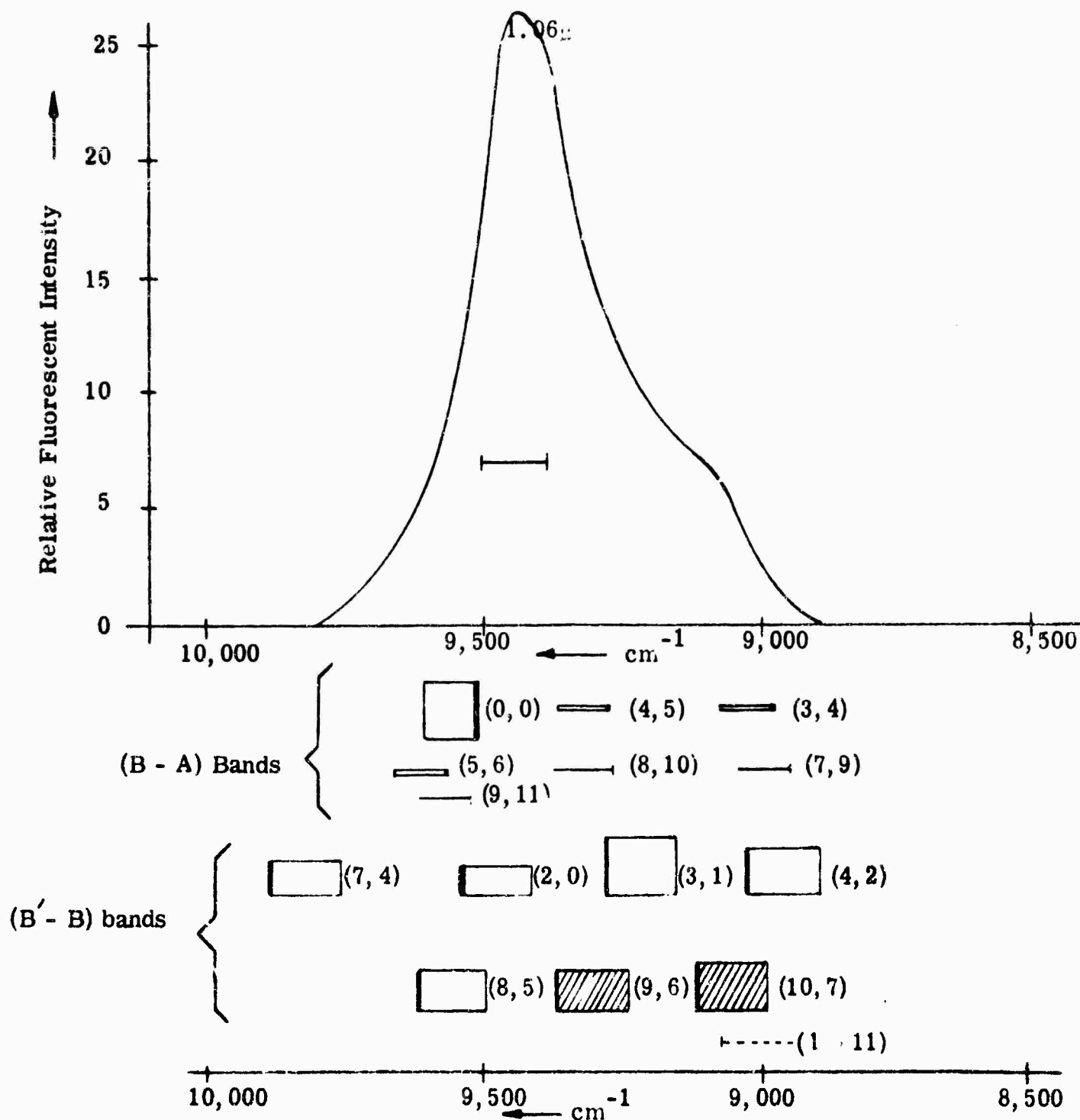


Figure 3. Nd and N₂ bands. The upper curve is the 1.06μ fluorescent band of Nd⁺⁺⁺ in a typical soda line glass at room temperature from Maurer (1963). The short horizontal bar in the center of this band indicates the range over which Snitzer (1965) obtains lasing when no restrictive interference plates are present within the resonant cavity. Below are indicated schematically the N₂·(B - A) and N₂·(B' - B) absorption bands which overlap the Nd fluorescence region. For each band the location of the P₁ head is emphasized by a heavier line. The relative heights of the band symbols for (B - A) show expected relative intensities. Similarly for the (B' - B) bands. However, the intensity scales used for these two band systems are not necessarily equal. The weak (B' - B) (1 → 11) band shown dotted at the bottom of the diagram is a case where absorption would be from N₂·B'(v = 1) upward to N₂·B(v = 11). The two shaded bands involve high levels of N₂·B' which are easily dissociable in collisions.

very close to the P_1 heads. From the photographs of several ($B' - B$) bands in the deep red region given by LeBlanc, Tanaka, and Jursa (1958), the most intense region of each band may be taken to stretch about 130 cm^{-1} toward decreasing wave-numbers from the P_1 head. The experimental wave-numbers given for the heads by these latter authors agree with the band origins calculated here for corresponding bands to within 15 cm^{-1} . The relative intensity estimates in ($B' - B$) were made from the appearance of the potential curves of the two states in Figure 2, in light of the Franck-Condon principle, and by comparison with LeBlanc, Tanaka, and Jursa's intensities for the deep red bands. The weak band at the bottom of Figure 3 represents a transition near 1.06μ where the B vibrational level lies above the B' vibrational level.

2.3 Possible Pumping and Lasing Bands

The most obvious place to try to set up a pump-lase transformer cycle would seem to be in the $(0, 0)$ band of $N_2 \cdot (B - A)$. This is the strongest available band of its system, and it lies very close to the wave-number region for which the most efficient Nd glass lasing mode has already been explored.

One potential drawback to the use of the $(0, 0)$ band is that probably considerable numbers of $N_2 \cdot B$ molecules in $(v = 0)$ would absorb a second Nd quantum to populate $(v = 2)$ of $N_2 \cdot B'$. Of potentially greater

importance is that lasing within the transformer might be hindered by absorption of emitted quanta in the $(B' - B) (2, 0)$ transition.

Another drawback might be that it would probably not be practical to "prepare" a sufficient population of nitrogen molecules in $(v = 0)$ of $N_2 \cdot A$ before the power flash by simply irradiating nitrogen gas with a flash of ultraviolet light. The $(0, 0)$ Vegard-Kaplan absorption band must be extremely weak in nitrogen gas at practical temperatures. Probably it would be best to raise molecules to $N_2 \cdot A (v = 0)$ by collisions with other atoms or molecules which had themselves been raised to an excited level near $50,000 \text{ cm}^{-1}$ through absorption of a preparatory UV flash in a strongly allowed transition. Possibilities for such an arrangement have not yet been explored under this contract.

The next most obvious place* for a pump-lase cycle would be in the $(4, 5)$ band. This band is weaker than $(0, 0)$ by about a factor of 13, but it occurs equally close to the best known region for Nd glass lasing. Although the $(5, 0)$ Vegard-Kaplan band surely is less intense than the known $(6, 0)$ and $(7, 0)$ bands, it might prove adequate for creating $N_2 \cdot A (v = 5)$ molecules, if an intense preparatory flash in its region around 1770\AA could be used. Figure 3 indicates that no appreciable numbers of $N_2 \cdot B (v = 4)$ molecules could reach the B' state by absorption of a second Nd laser light quantum.

* One is restricted to the 1st Pos. bands for the main power cycle, in the simplest cases at least. If the main Nd laser pumping wavelength was instead placed at one of the $(B' - B)$ bands, with previous preparation of the molecules by absorption of UV light in one of the $(B' - X)$ bands, an adequate B population could not be maintained in the face of B to A leakage by fluorescence — unless simultaneous $(B' - B)$ and $(B - A)$ pump-lase transformer cycles were being operated.

The (5, 6) band of (B -- A) is of about the same strength as the (4, 5) although less advantageously placed with respect to the Nd emission. Nitrogen molecules in $N_2 \cdot A$ ($v = 6$) could be prepared by an ultraviolet flash in the known V-K band. However, second Nd quantum absorption and lasing light absorption would certainly be present raising considerable numbers of molecules into ($v = 8$) of $N_2 \cdot B'$. It may be noted that nitrogen molecules in ($v = 9$) and slightly higher vibrational levels of B' are known to have a rather strong tendency toward dissociation of the molecule upon subsequent collisions. (Bayes and Kistiakowsky, (1960).)

Absorption in the ($B' - B$) bands would cause no real trouble if these transitions could be expected to either (a) saturate after the first few microseconds in a very high flux environment, or (b) set up their own parallel pump-lase cycles. One of these alternatives would certainly occur if only optical transitions were involved. However, at any time when considerable numbers of nitrogen molecules are in vibration levels above ($v = 0$) in any one of the electronic states, the phenomenon of vibrational exchange upon collision between molecules will produce a distribution of population over many other vibrational levels adjacent to the original ones. In order to reduce the probabilities for vibrational exchange, the transformer medium should probably be operated at as low a temperature as possible — or about 80°K in this case of nitrogen. Another process

tending to diffuse the populations occurs whenever molecules are placed in any level higher than $N_2 \cdot B (v = 0)$. There is then a quite appreciable probability for collisions to transfer a molecule to one of the other nearby electronic states. Such a process might occur even for $N_2 \cdot B (v = 0)$ if $^3\Delta_1$ actually falls as low as is sketched in Figure 2. Thirdly, even when cycling wholly within the (0, 0) band, fluorescence downward from $N_2 \cdot B (v = 0)$ will always produce appreciable concentrations in $N \cdot A_2$ vibration levels as high as at least ($v = 3$), as may be seen from Table 1.

The complexities resulting from this spreading out of the populations, although not necessarily deleterious for the transformer laser, cannot be analyzed in advance with our present incomplete knowledge of the many collision parameters involved.

Table 1 shows that molecular refrigeration based on the center of gravity of fluorescence falling at shorter wavelength than the pumping light will not be available when operating a cycle within the (0, 0) band, although it would be when operating on the (4, 5) band. However, broadening of the vibrational population distribution, as a result of vibrational exchange collisions or collisions populating other electronic states, could easily alter the center of gravity of the total fluorescence.

Of course, all of the above discussion is predicated on an assumption that molecules once placed in $N_2 \cdot A$ or $N_2 \cdot B$, or perhaps $N_2 \cdot B'$ or the other

$\frac{V_A}{V_{11}}$	0	1	2	3	4	5	6	7	8	9	10	11	12
0	9 512.10 1000	8 079.28 434	6 574.05 154	5 296.68 24	3 947.06 1.2	2 625.37 0.1	1 331.83 0.0						
1	11217.26 1260	9 784.42 6.5	8 379.21 261	7 001.84 171	5 652.22 98	4 330.53 11	3 036.99 1.2	1 771.85 0.1	535.23 0.0				
2	12 893.57 719	11 460.76 862	10 055.55 214	8 678.18 102	7 328.56 126	6 006.87 81	4 713.33 18	3 448.19 3.3	2 211.37 0.3	1 033.92 0.0			
3	14 540.94 142	13 105.12 833	11 702.91 305	10 325.54 271	8 975.92 102	7 654.23 97	6 360.69 100	5 095.55 17	3 858.93 5.2	2 651.28 1.0	1 473.25 0.1	253.90	
4	16 159.10 57	14 725.50 335	13 321.32 372	11 943.38 95	10 594.36 252	9 272.57 19	7 979.13 2	6 713.99 4	5 477.37 7	4 269.72 3.3	3 091.89 0.9	1 872.34 0.0	824.80
5	17 748.65 9	16 315.81 73	14 910.60 504	13 533.23 520	12 183.61 93	10 861.92 180	9 568.38 80	8 303.24 16	7 066.62 0	5 858.97 2.2	4 680.94 2.5	3 461.59 1.0	2 414.05 0.2
6	19 308.90 0	17 876.06 13	16 470.85 111	15 093.43 548	13 743.86 362	12 422.17 134	11 128.63 2.6	9 862.49 44	8 626.87 23	7 419.22 2.4	6 241.19 0.2	5 021.84 1.0	3 974.30 0.7
7	20 839.96	19 407.12	18 001.91 17	16 624.54 154	15 274.92 506	13 953.23 161	12 659.69 166	11 394.55 4	10 157.93 18	8 950.28 21	7 712.25 5.6	6 522.90 0.2	5 505.36 0.2
8		20 908.75	19 503.67	18 126.30 29	16 776.68 193	15 454.99 408	14 161.45 0	12 896.31 40	11 659.69 7.9	10 452.04 1.5	9 274.01 6.1	8 064.66 3.1	7 007.12 0.5
9			20 975.92	19 598.55 6	18 248.93 39	16 927.24 218	15 633.73 318	14 368.56 15	13 131.94 49	11 924.29 29	10 746.26 0.0	9 526.91 6	8 479.37 7
10				21 041.28	19 691.66 9	18 369.97 41	17 076.43 210	15 811.29 211	14 574.67 39	13 367.02 18	12 188.99 28	10 969.54 3.1	9 922.10 1.2
11					21 104.70	19 783.01 8	18 489.47 46	17 224.26 210	15 987.74 131	14 780.06 45	13 602.03 4.0	12 382.68 20	11 335.14 5
12						21 166.10	19 872.56 12	18 607.42 52	17 370.82 170	16 163.20 13	14 985.12 34	13 765.77 0.0	12 718.23 9

TABLE 1. LOCATION (IN CM^{-1}) OF THE P_1 HEADS OF THE NITROGEN FIRST POSITIVE BANDS, WITH ESTIMATES OF RELATIVE INTENSITY. DATA FROM DIKKE AND HEATH (1959).

excited states, will not be forced back to the ground state too frequently by any of the collision processes. Discussion of this basic assumption, that the quenching rate is tolerable, is postponed to a later section of this report.

In summary, sufficient experimental data are not available yet to decide which band of the nitrogen First Positive System might provide the best transformer arrangement for pumping with Nd glass lasers. However, as a typical example, the properties of the (0,0) band of this system will be considered in the next sections.

3. STRUCTURE OF THE NITROGEN FIRST POSITIVE BANDS.

3.1 Rotational Levels of $N_2 \cdot A(v = 0)$

The first excited electronic state A of the nitrogen molecule is a ${}^3\Sigma_u^+$ state. As with all Σ states, $N_2 \cdot A$ follows Hund's coupling case (b) with the quantum number K taking all integral values from zero upward, within each vibrational state.* The lowest level, with $K = 0$, is always single and has total angular momentum vector $J = 1$. Each higher K-value corresponds to a very close triplet of levels having $J = K - 1$, K , and $K + 1$ respectively.

For each vibrational state the members of the triplets with $J = K$ form a series whose energies approximately follow the usual simple formula. In the vibrational state ($v = 0$) with values of $K \geq 1$ this is

$$F_{J=K}(v = 0) = B_0 K(K + 1) - D_0 K^2(K + 1)^2 + \dots$$

for which Dieke and Heath (1959) determined the value $B_0 = 1.4457 \text{ cm}^{-1}$ and accepted the value $D_0 = 5.84 \times 10^{-6} \text{ cm}^{-1}$ from Carroll (1952). Approximate theoretical formulas for the separations among the "spin triplets" are given

* Some recent authors use the symbol N, instead of K, for this quantum number.

in Herzberg's book.*

Dieke and Heath's experimental levels up to $K = 20$ for ($v = 0$) are shown in Figure 4. The experimental spin triplet separations, being less than 3 cm^{-1} everywhere, are too small to illustrate in this Figure, although the order in which the J -values were found to occur energetically is indicated. The (+, -) and (a, s) symmetry characters of the levels are also marked on the diagram. In any $^3\Sigma_u^+$ electronic state of a homonuclear diatomic molecule, rotational levels of even K have the symmetry characters + and a, with the reverse for levels of odd K .

3.2 Rotational Levels of $N_2 \cdot B(v = 0)$

The second excited electronic state B of the nitrogen molecule is a $^3\Pi_g$ state. At high rotation levels this state also follows Hund's coupling case (L), with the quantum number K taking on integral values. For each K there occurs $J = K-1$, $J = K$, and $J = K+1$, with separations between them of the order of 15 cm^{-1} or less. Finally, each one of these three is a close Λ -type doublet, as is true for all electronic Π states. The Λ -doubling amounts to less than 3 cm^{-1} separation, except for very high rotation levels. Figure 5 shows the energy level as high as $K = 16$ for the vibrational state ($v = 0$) as found by Dieke and Heath, with the Λ -doubling being indicated only schematically.

* G. Herzberg, "Molecular Spectra and Molecular Structure. I Spectra of Diatomic Molecules", Van Nostrand, 2nd ed., 1950. This standard reference will be referred to throughout this report simply as "Herzberg's book".

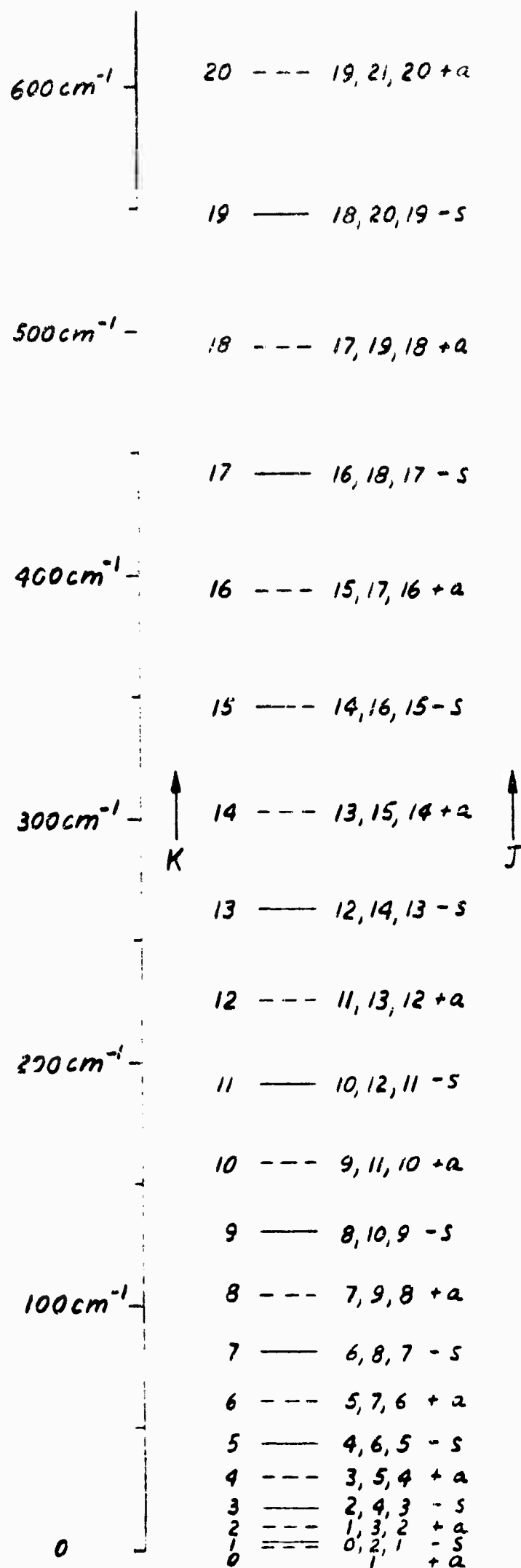


Figure 4. Experimental locations of rotational levels for $N_2 \cdot A$ ($v = 0$). Those with the symmetry character a are shown dotted. For each unresolved triplet, J values are written from left to right in order of decreasing energy.

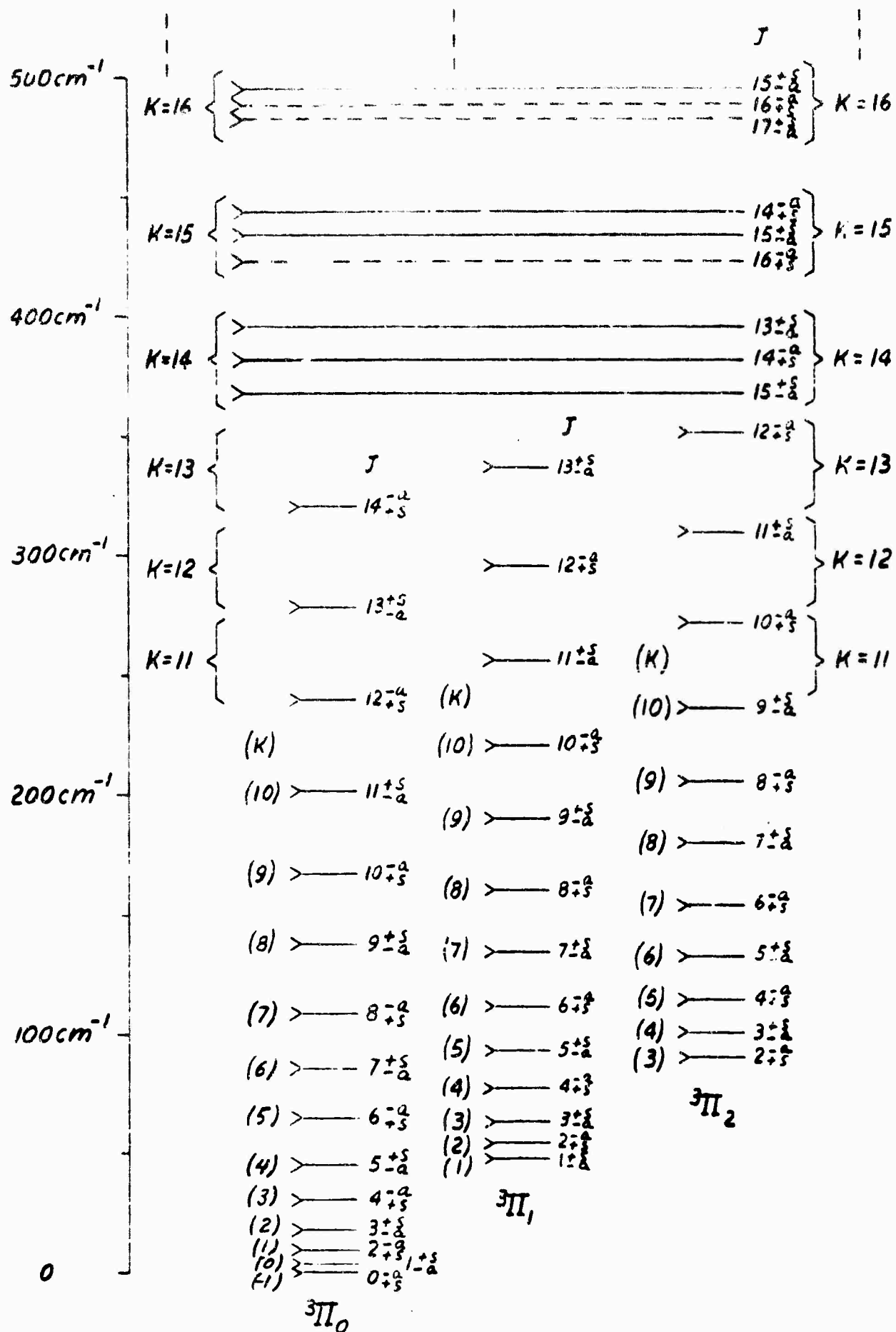


Figure 5. Experimental locations for rotational levels of $N_2^+ B(v=0)$. The zero of energy chosen for this diagram lies 9510.67 cm^{-1} above that of Figure 4. Dotted levels are estimated locations not measured experimentally by Dieke and Heath.

At low rotation levels, below the neighborhood of about $K = 11$, the state goes over to Hund's coupling case (a), where K loses its physical meaning and is no longer a good quantum number. The levels of various J -values, each still a Λ -doublet, regroup themselves energetically into three sequences, to which may be assigned the labels ${}^3\Pi_0$, ${}^3\Pi_1$, and ${}^3\Pi_2$. This gradual change in the level pattern upon going toward lower energies is apparent in Figure 5. In each of these sequences the minimum value of J is equal to the subscript in the sequence label.

Herzberg's book describes the rather complex approximate theoretical formulas which have been derived to represent the energy values of such a system of ${}^3\Pi$ levels. The only simple relationship which is reasonably exact is that the center of gravity of all six levels belonging to any one value of $J \geq 2$ is given for all rotations by

$$B[6J(J + 1) - 2] + \text{const.}$$

From their experimental levels, Dieke and Heath derived the value $B_0 = 1.62849 \text{ cm}^{-1}$ in this formula, for the ($v = 0$) vibrational state.

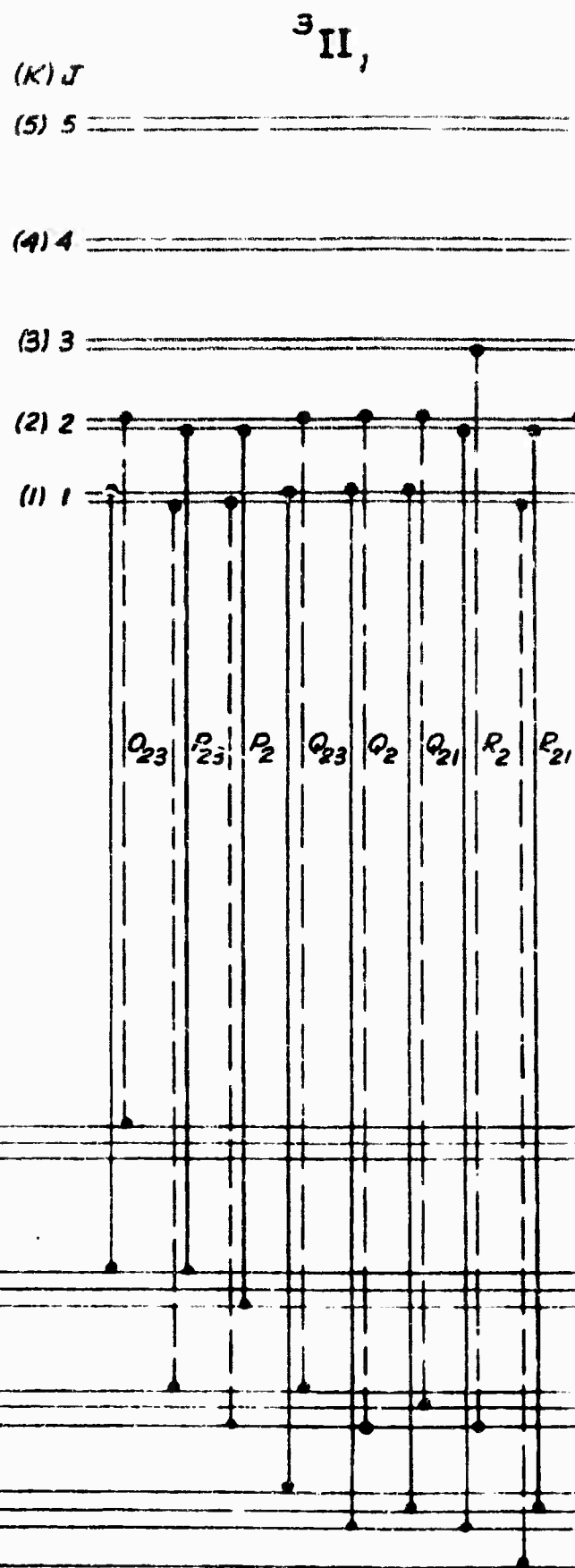
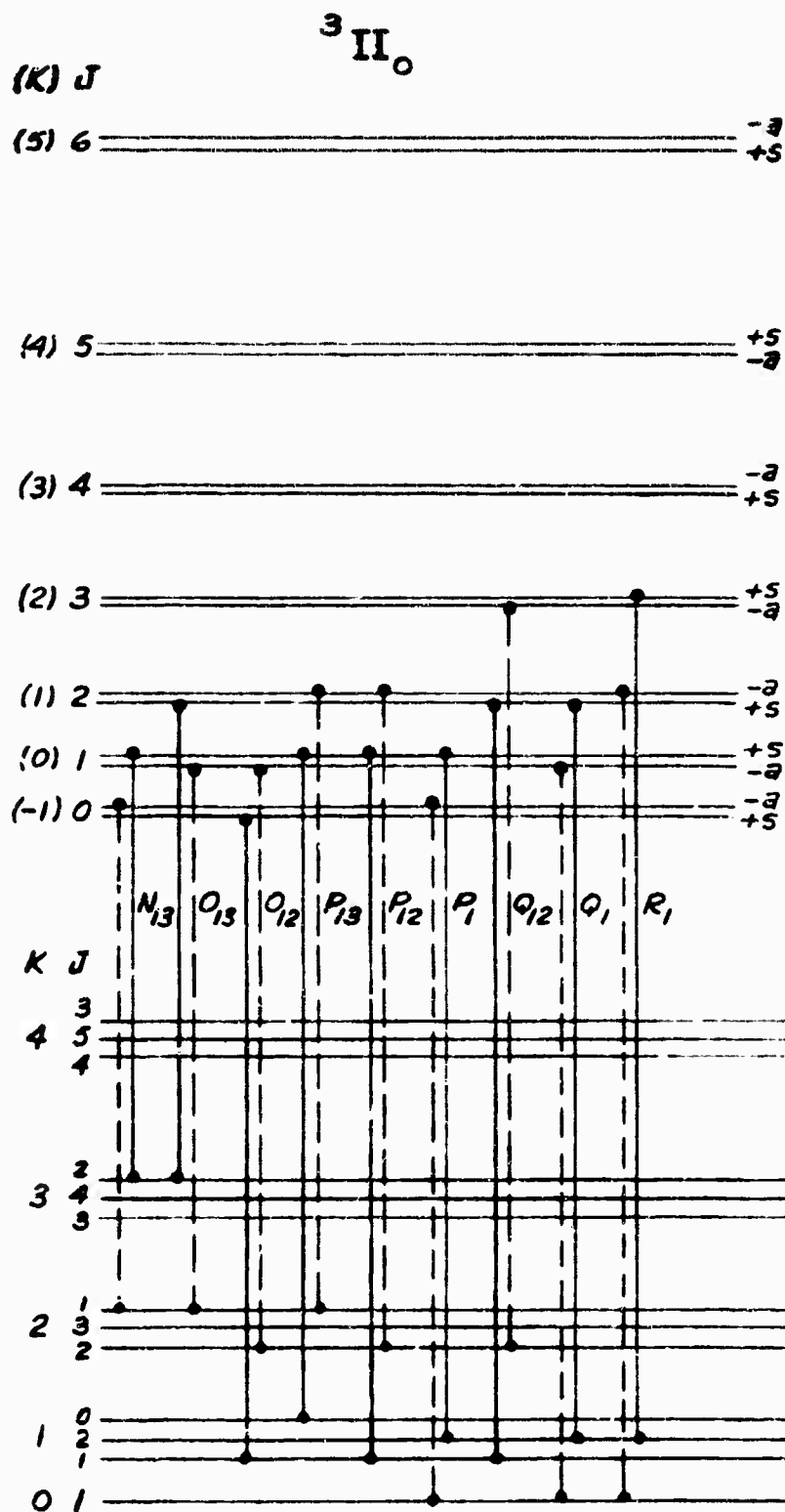
It will be convenient in distinguishing the spectrum lines later, to extend the numeration of levels by K -values in a smooth sequence down into the low rotation regime, even though K is not a good quantum number there and has no physical meaning. Such level labels have been applied in Figure 5.

In every $^3\Pi$ electronic state, the two components of each Λ -type doublet will have opposite \pm symmetry characters. In some such molecular states all levels of even J may have their plus Λ -components lying lower energetically than their minus Λ -components, and vice versa for levels of odd J . In other $^3\Pi$ molecular levels these relations are reversed. Dieke and Heath found the former situation in $N_2^+ B$, as indicated in the diagram. For all $^3\Pi_g$ in homonuclear molecules, the $+$ levels also carry the symmetry character s.

3.3 The Rotational Branches of the $N_2^+ (B - A)$ Bands

For a given vibrational transition, such as in the (0, 0) band, the rotational selection rules allow in principle any optical transition which (a) has $\Delta J = \pm 1$ or 0, with the transition $J = 0$ to $J = 0$ being forbidden, (b) combines a $+$ with a $-$ level, and (c) combines an s with an s level, or an a with an a level. Inspection of the level diagrams already given for the $^3\Pi$ and $^3\Sigma$ states of nitrogen will show that the multitude of possible transitions allowed by these rules may be organized into 27 different classes. Figure 6 shows the labelling system adopted by Dieke and Heath to define these 27 branches of a rotation-vibration band in the $N_2^+ (B - A)$ system*. Within each branch, Dieke and Heath label each spectrum line by the K-value of its lower level. We will write these K-values of the labels in parentheses — as for the $Q_{23} (10)$ line of the (0, 0) band.

* Herzberg's book, and some other authors, use a different nomenclature for the branches and lines of a $^3\Pi - ^3\Sigma$ band.



A

Approximate theoretical intensity relations among the lines of the various branches are discussed in Herzberg's book, for conventional methods of excitation. In the low rotation region, lines of all 27 branches are usually observable under most experimental conditions. However, at high rotations where K is a good quantum number, there is no appreciable intensity except in lines following additional selection rules involving ΔK . These have the effect of permitting observable intensity for the high rotation lines of only those branches with a single subscript in their label in Figure 6.

Since N_2^{14} is a homonuclear molecule, symmetry relations will cause adjacent lines in every branch to be alternately weak and strong — under conventional means of excitation in naturally occurring nitrogen gas. The usual approximate neighboring intensity is 2:1 and the lines labelled by odd, K -values in parentheses are the strong ones. The strong lines are transitions between two levels of s symmetry. The weak lines are transitions between two levels of a symmetry.

The actual (0, 0) band of the $N_2 \cdot (B - A)$ system has never been specifically analyzed experimentally, although it has often been observed at low to moderate resolution. The $N_2 \cdot B$ ($v = 0$) and $N_2 \cdot A$ ($v = 0$) level locations illustrated in Figures 4 and 5 were determined by Dieke and Heath from other bands involving these vibrational states, such as the (1, 0),

(2, 0), and (3, 0) bands of $N_2 \cdot (B \leftarrow A)$ and the (0, 0) band of the $N_2 \cdot (C \leftarrow B)$ system. These known level positions will permit calculation of wavenumbers of the (0, 0) lines for $N_2 \cdot (B \leftarrow A)$ by simple subtraction, using the diagram in Figure 6 as a guide for the selection rules and the labelling.

As a preliminary step, Figure 7 displays a chart of the analogous (1, 0) band, as constructed directly from Dieke and Heath's tables of measured wavenumbers. The heights shown for the lines are proportional to Dieke and Heath's rough estimates of relative intensity on a 0 to 10 scale, in the emission spectrum from a low pressure nitrogen discharge tube immersed in liquid nitrogen. Relative intensities can well be different for other types of emission or absorption arrangements. At this low gas temperature none of the rotational branches was observable beyond line (18).

It will be noted that the $N_2 \cdot (B \leftarrow A)$ bands degrade toward the violet, in contrast to the majority of diatomic molecule bands, which degrade toward the red. Such an appearance is a consequence of the average internuclear distance in electronic state B being less than it is in state A. As a result, the rotational spacing constants — as B_0 , for example — are larger in the upper state than in the lower. The reverse is true for the majority of band systems of diatomic molecules, as $N_2 \cdot (B' \leftarrow B)$ for example.

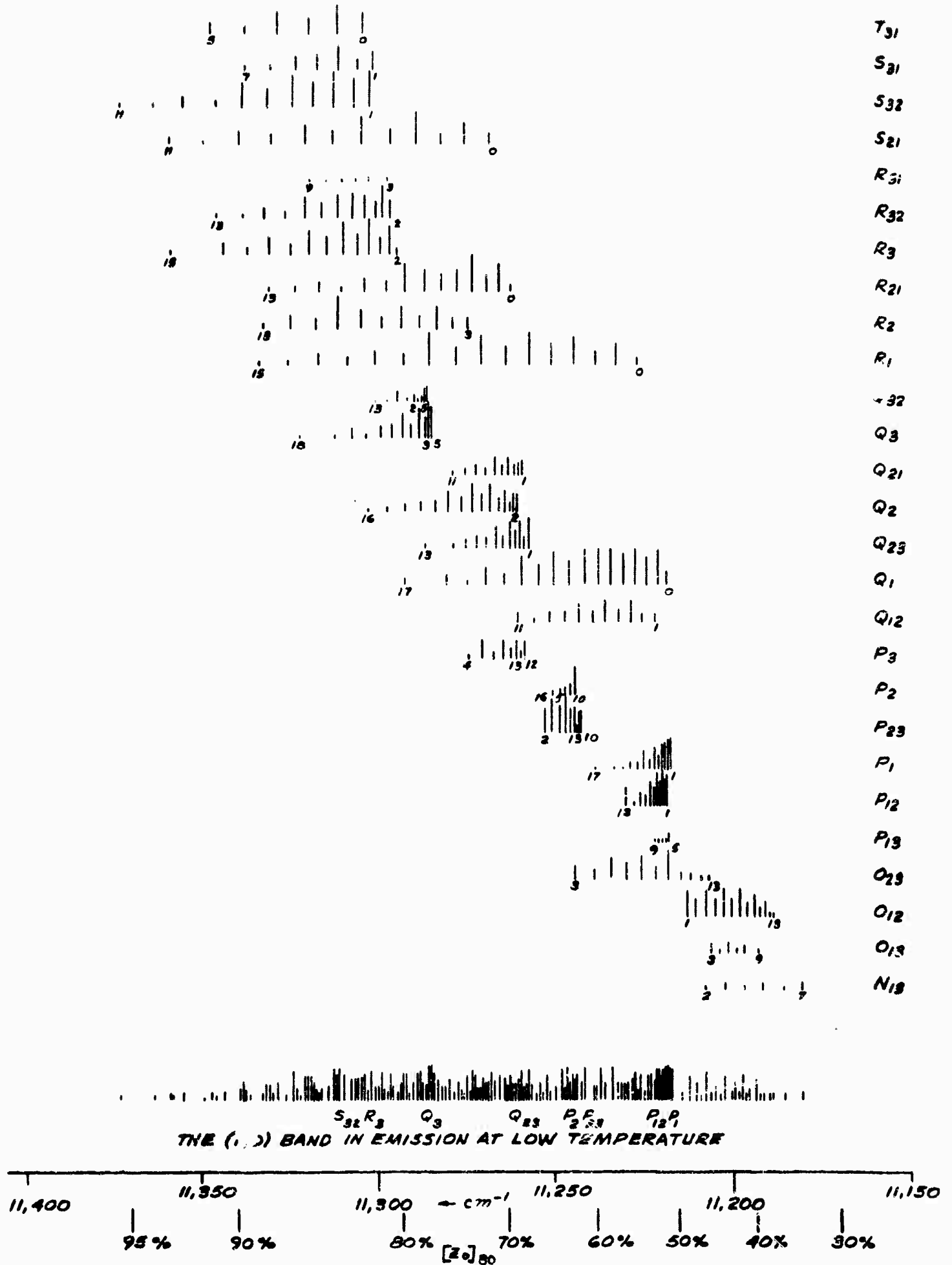


Figure 7. The Low-Pressure Discharge Spectrum of the (1, 0) Band of N₂ • (B ~ A) at Low Temperature

4. LASING POSSIBILITIES IN THE (0,0) BAND AT 80° K

4.1 80° K Boltzmann Rotational Distribution for ($v = 0$) in $N_2 \cdot A$ and $N_2 \cdot B$

Collisions of a given nitrogen molecule with another molecule of any kind, or with any atom, are known to cause changes in the rotational angular momentum of the nitrogen molecule quite readily. Values of J and K are often changed by several units in each collision, with some rotational energy often going into or coming from the store of translational energy of the assemblage.

However, it is found that collisions only extremely rarely move a nitrogen molecule from an s level into an a level, or vice versa. A volume of nitrogen gas behaves almost as if it were a mixture of two quite separate kinds of nitrogen. One kind tends to keep all its molecules in rotational levels of s symmetry, and the other kind tends to keep all its molecules in levels of a symmetry. The concentration ratio of the two types in any given volume at a certain moment will depend on the prior history of the gas, but this ratio will remain almost constant despite collisions or despite the presence of optical radiation, for a very long time.

This means that for any one vibrational state of either $N_2 \cdot A$ or $N_2 \cdot B$, two separate and almost completely non-connected rotational equilibrium population distributions should be calculated -- one for the molecules in levels of s symmetry, and one for the molecules in levels of a symmetry. In each case the zero of relative energies is to be taken at the lowest occurring level

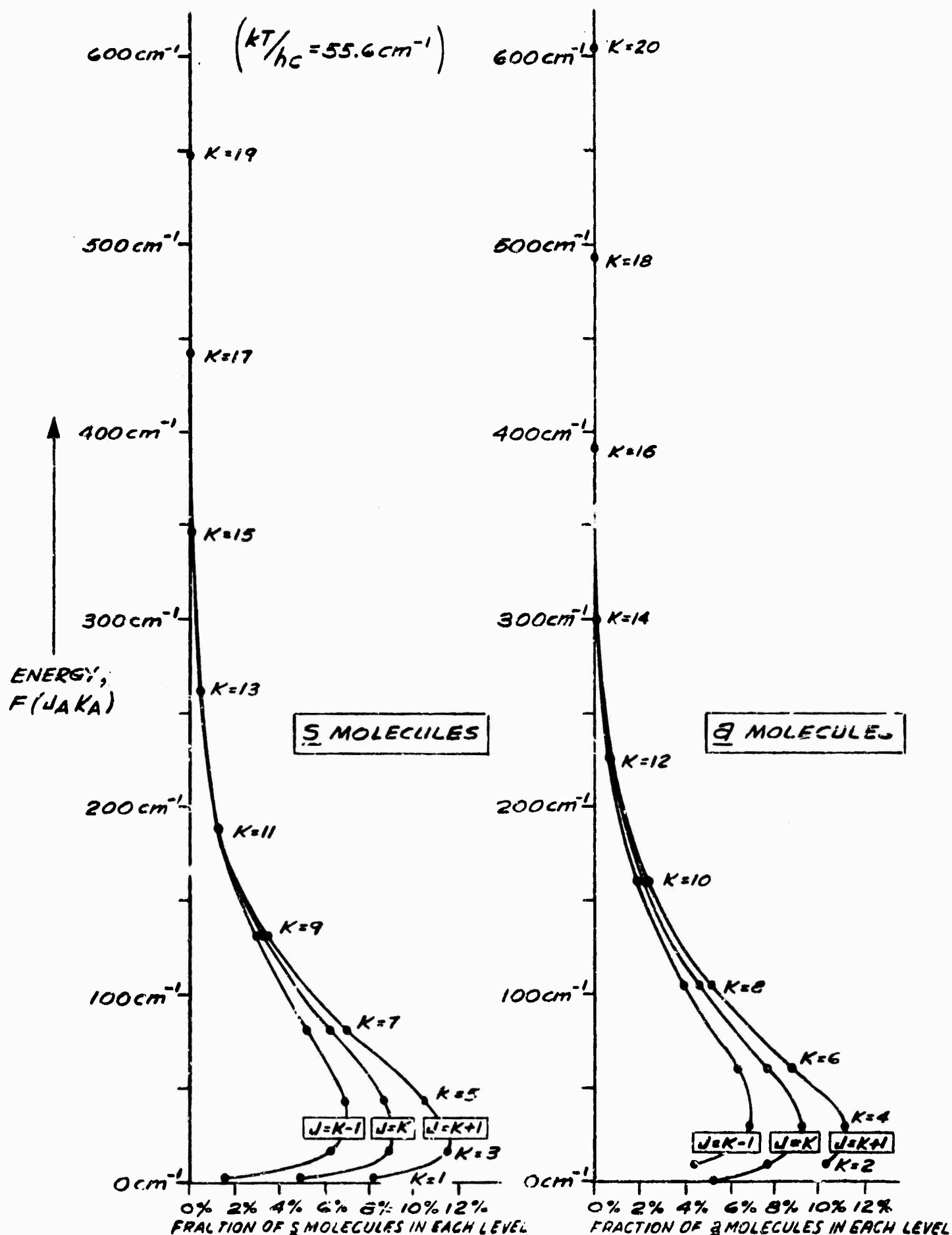
of the particular symmetry being considered for all problems involving times of milliseconds or less. With the relative energy $F(JK)$ of any chosen rotational level being defined in this way, the fraction of the total molecules of one symmetry type in the vibrational state which will be in the chosen rotational level, in the presence of complete rotation-translation equilibrium at gas temperature $T^\circ\text{K}$, is given by the usual Boltzmann formula

$$n(JK) = \frac{(2J + 1)e^{-F(JK)hc/kT}}{\sum_{\underline{s} \text{ or } \underline{a}} [(2J + 1)e^{-F(JK)hc/kT}]},$$

where the sum in the denominator is over all levels in the vibration state which have the same symmetry type as the particular rotational level in question.

Figure 8 shows such relative rotational distributions calculated for the \underline{s} and \underline{a} populations of $\text{N}_2^+ \text{A}$ ($v = 0$) at 80°K , based on the Dieke and Heath level locations sketched in Figure 4. Reduction of vibrational exchange probabilities constitutes one reason for choosing 80°K as a possible operating temperature of interest for the transformer gas volume. It will be noted that most of the molecules are in levels below about $K = 10$ under these conditions.

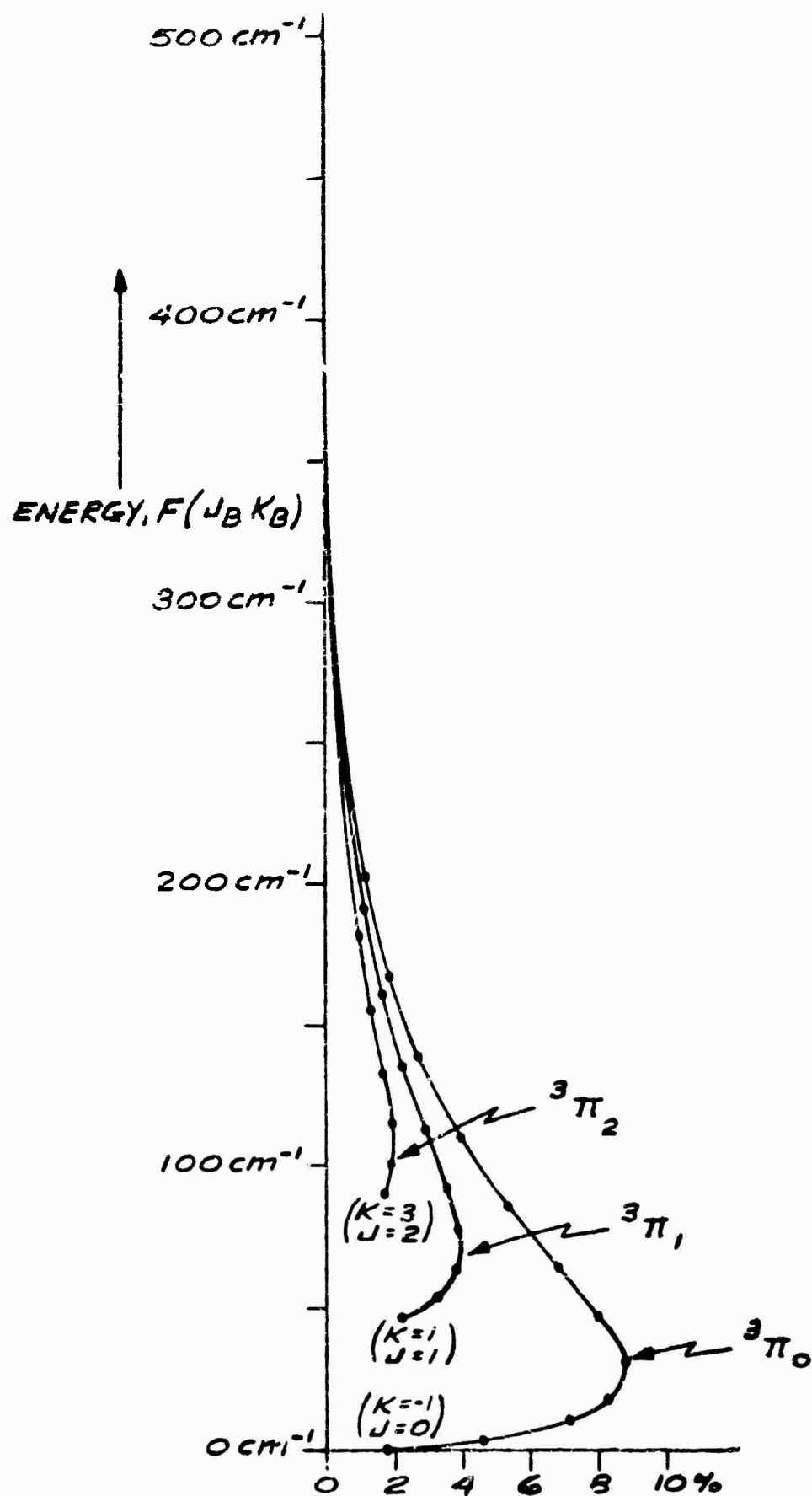
In a $^3\Sigma$ state, collisions can quite readily alter both J and K for a molecule in any level, so that all the types of \underline{s} levels, for example, must be lumped together in calculating the distribution of \underline{s} molecules. Nevertheless,

Figure 8. $80^\circ K$ Boltzmann Rotational Distribution for N_2 . A ($v = 0$)

the s distribution curve has three distinguishable branches at low rotations. These contain levels with $J = K - 1$, $J = K$, or $J = K + 1$, respectively, which differ because the spin triplets are levels of almost equal energy but considerably different $(2J + 1)$, in the low rotation region. Any transient approach to equilibrium should occur simultaneously in all three branches, under most conventional experimental conditions. The distribution of a molecules behaves in similar fashion.

Figure 9 shows corresponding relative rotational population distribution curves for Boltzmann equilibrium at 80°K in $N_2 \cdot B(v = 0)$. Again, all the levels of s symmetry are to be considered as one group in calculating a true Boltzmann equilibrium distribution of whatever s molecules are present in this vibrational level. A similar calculation of the equilibrium distribution of a molecules over the rotational levels having a symmetry produces a set of curves which cannot be distinguished from the s curves on the scale of Figure 6, since the Λ -doubling is very slight.

As before, each of the distributions has three branches in the low rotation region, because levels of different $(2J + 1)$ fall at similar energies. However, these three branches for low rotations have an additional importance in the case of the $^3\Pi$ state. Although there are no experimental data specifically for nitrogen, it seems probable that collisions cannot as readily move a low rotation nitrogen molecule from levels of $^3\Pi_0$ into levels of $^3\Pi_1$, for example, as they do into other levels of $^3\Pi_0$. Thus, in an analogous case of



FRACTION (%) OF \underline{S} MOLECULES IN EACH LEVEL OF \underline{S} SYMMETRY
OR
FRACTION (%) OF \underline{B} MOLECULES IN EACH LEVEL OF \underline{B} SYMMETRY

Figure 9. $80^\circ K$ Rotational Boltzmann Distribution for $N_2 \cdot B$ ($v = 0$)

NO-He collisions at 300°K, Broida and Carrington (1963) observed that collisions shifting an NO molecule between $^2\Pi_{1/2}$ and $^2\Pi_{1/2}$ levels only 0.02 cm^{-1} apart occurred an order of magnitude less frequently than collisions which shifted the molecule between rotation levels of $^2\Pi_{1/2}$, which were as much as 50 cm^{-1} apart. This means that in any transient situation, collisions will move the molecules up and down the three columns of levels in the low rotation region of Figure 5 considerably more readily than they will move them from one column to another. Whenever enough time has elapsed for a stationary Boltzmann equilibrium among molecules of a given symmetry to be reached, the curves of Figure 9 will apply.

4.2 Equilibrium Excitation for Zero-Gain at Each (0, 0) Line Wavelength

We now calculate fractional excitations $[Z_0]_{80}$ required for zero-gain at Boltzmann rotational equilibrium in the lines of the (0, 0) band at 80°K. The definition of Z_0 must differ slightly from the one used with the CN molecule, because of the additional symmetry characters attached to the N_2 levels.

We define $[Z_0]_{80}$ for any chosen transition between a pair of \underline{s} levels in the band as that fraction of the total number of \underline{s} molecules in $N_2 \cdot A(v = 0)$ plus $N_2 \cdot B(v = 0)$ which must be in $N_2 \cdot B(v = 0)$, with Boltzmann rotational equilibrium present in both upper and lower vibration states, in order that zero-gain occur for a beam of light sent through the gas at the wavelength of the chosen transition.

Likewise, $\left[Z_0 \right]_{80}$ is defined for a transition between a pair of a levels as that fraction of the total number of a molecules in the two vibration states which must be excited to the upper vibration state for a similar result. As already mentioned, in every branch of the band those spectrum lines labelled with an odd number in parentheses will involve only the s molecules, while those labelled with even K will involve only a molecules.

As is evident from the derivation given in Report GPL A-31-1, a general formula for the Z_0 of any line in the (0, 0) band may be written as

$$\left[Z_0 \right]_{80} = \left[\frac{N_{A0}(J_A K_A) \cdot g(J_B)}{n_{A0}(J_A K_A) \cdot g(J_B) + n_{B0}(J_B K_B) \cdot g(J_A)} \right]_{80}$$

where $n_{A0}(J_A K_A)$ = the fraction of the molecules of appropriate symmetry type in vibration state ($v = 0$) of $N_2 \cdot A$, which will be in the lower level of the chosen transition when Boltzmann rotational equilibrium at 80°K is present (illustrated in Figure 8),

$n_{B0}(J_B K_B)$ = the fraction of the molecules of this symmetry type in vibration state ($v = 0$) of $N_2 \cdot B$, which will reside in the upper level of the chosen transition in similar equilibrium (illustrated in Figure 9),

$g(J_A) = (2J + 1)$ for the lower level of the transition, and

$g(J_B) = (2J + 1)$ for the upper level.

As a sample calculation, the vibrational excitation fraction required for zero-gain in the $P_{12}(1)$ line with rotational equilibrium at 80°K is

$$s \left[P_{12}(1) Z_0 \right]_{80} = \left[\frac{4.944\% \times 3}{(4.944\% \times 3) + (4.652\% \times 3)} \right] = 0.515 \approx 52\%.$$

This means that under the conditions assumed zero-gain occurs for the $P_{12}(1)$ line, which lies near $10,510\text{\AA}$, at about 52% excitation.

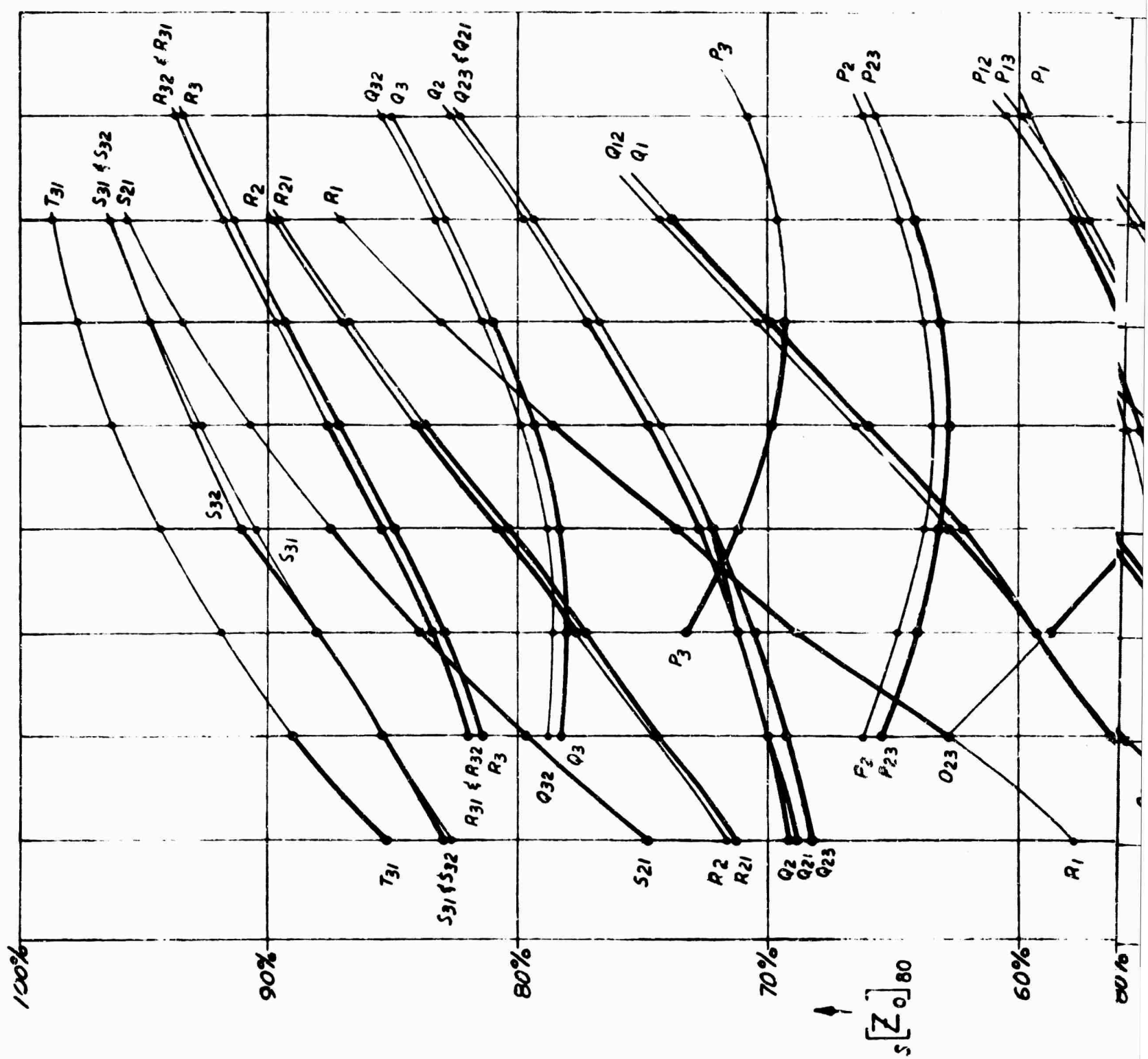
Figure 10 displays $\left[Z_0 \right]_{80}$ values calculated in this manner for s lines of all the branches in the (0,0) band. Still another set of 27 curves could be constructed for the a lines of this band in an entirely analogous fashion. Their pattern would not be noticeably different from Figure 10.

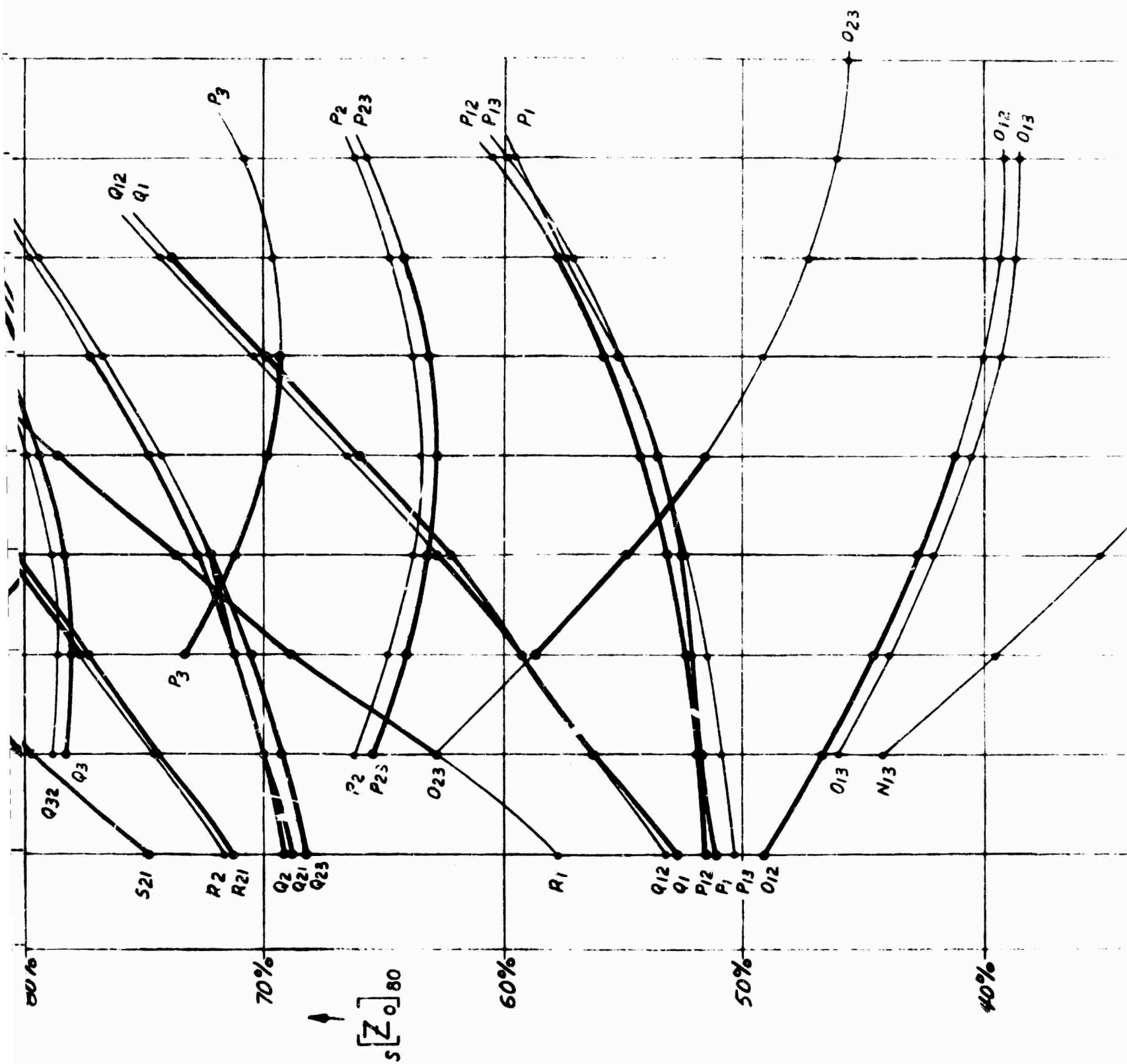
An alternative way of calculating $\left[Z_0 \right]_{80}$ for any line follows from substituting the Boltzmann equation for the n's into the formula which defines Z_0 . The result is

$$s \left[Z_0 \right]_{80} =$$

$$\left\{ \frac{(1/\Sigma_{sA}) \cdot g(J_A) \cdot g(J_B) \cdot e^{-F(J_A K_A)hc/kT}}{\left[(1/\Sigma_{sA}) \cdot g(J_A) \cdot g(J_B) \cdot e^{-F(J_A K_A)hc/kT} \right] + \left[(1/\Sigma_{sB}) \cdot g(J_B) \cdot g(J_A) \cdot e^{-F(J_B K_B)hc/kT} \right]} \right\}_{80}$$

$$= \left\{ \frac{1}{1 + (\Sigma_{sA}/\Sigma_{sB}) \cdot e^{-(\sigma_{sA} - \sigma_{sB})hc/kT}} \right\}_{80}$$





B

Figure

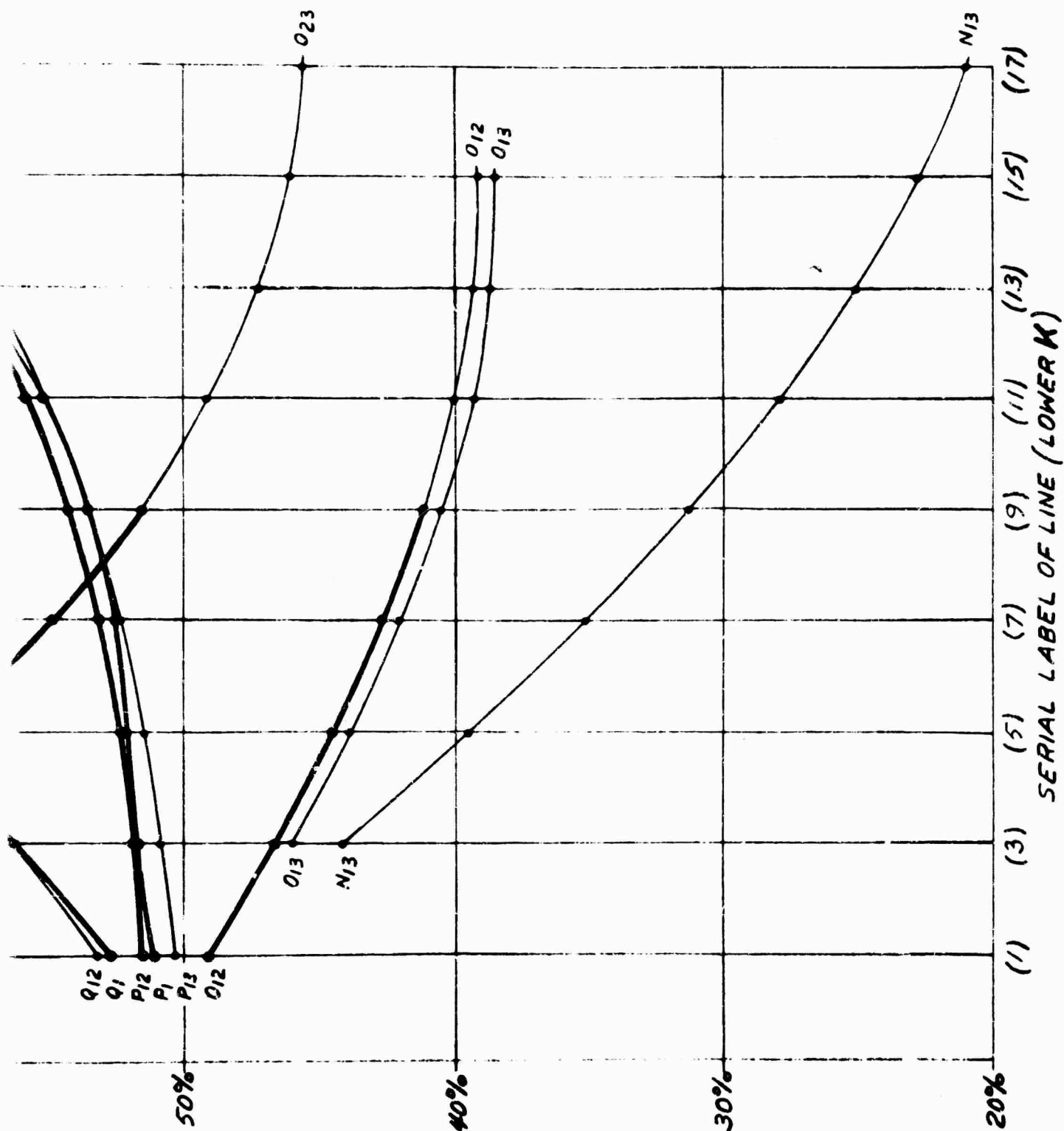


Figure 10. $[Z_0]_{80}$ for s lines of the (0, 0) Band.

C

The segments of the above curves which are accentuated in the drawing relate to the most intense spectral lines.

In this equation the Σ 's are the "state sums" which appear in the denominator of the Boltzmann formula for the \underline{n} 's, σ is the wavenumber of the spectrum line for which Z_0 is to be found, and σ_0 is the separation in wavenumbers between the zeros of the two relative energy scales by which $F(J_B K_B)$ and $F(J_A K_A)$ were separated — which equals the wavenumber of the O_{12} (1) spectrum line in $N_2 \cdot (B - A)$ bands. An analogous formula gives $\left[Z_0 \right]_{\sigma_0}^{\sigma_a}$ with σ_{a0} equalling the wavenumber of the $P_1(0)$ line for $N_2 \cdot (B - A)$, which in the case of the (0, 0) band is only 4.50 cm^{-1} greater than σ_{s0} .

It thus appears that Z_0 is a monotonic function of wavelength for all the lines of one symmetry class throughout a given electronic-vibration-rotation band of a diatomic molecule at a chosen temperature. Furthermore, the form of the expression is such that Z_0 always decreases as one goes toward longer wavelengths, regardless of the particular values of the diatomic molecule constants or of the temperature, within a given vibronic band.

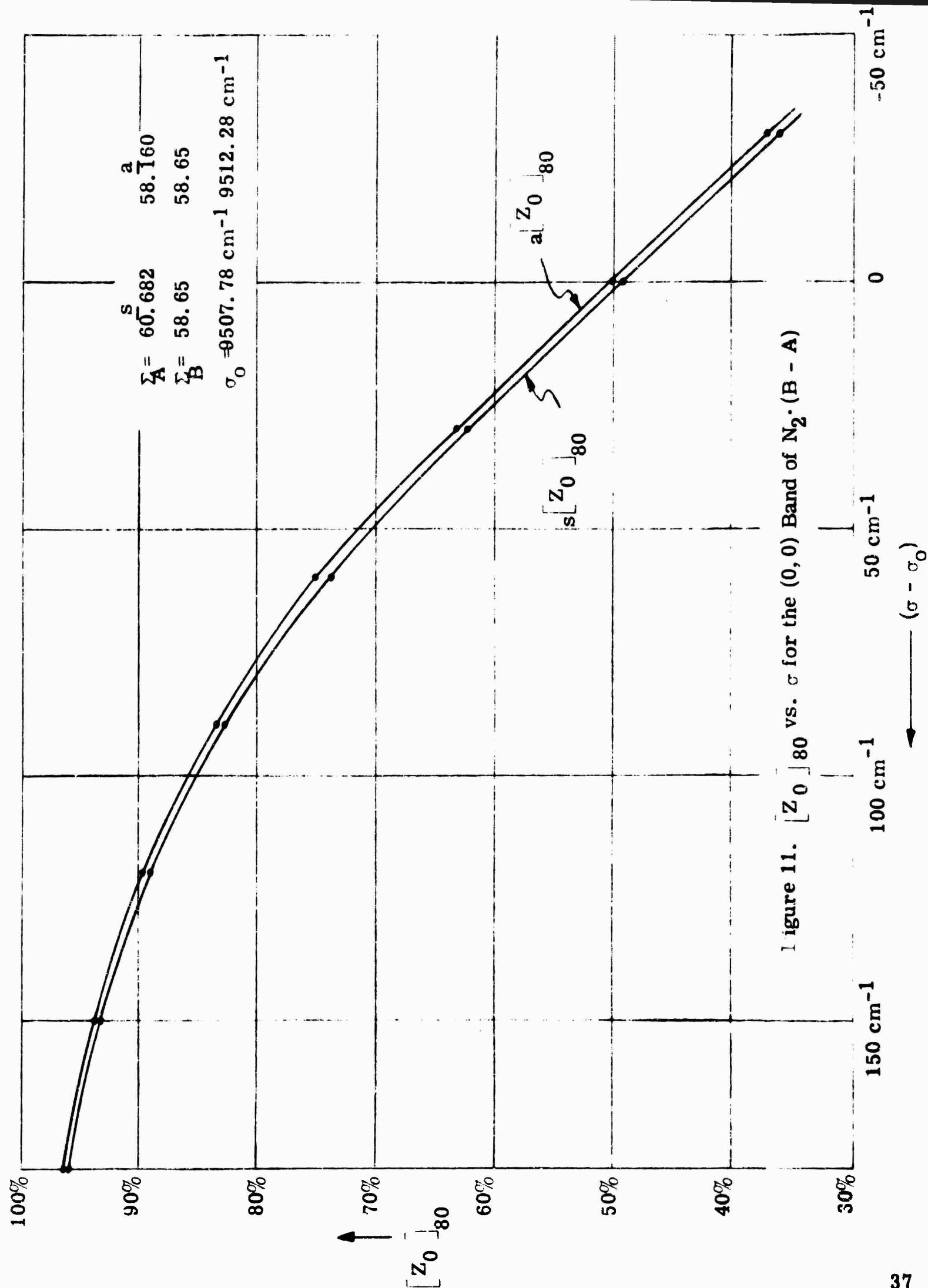
In other words, pumping practically to transparency in any lines near the shorter-wave side of any vibronic band of any diatomic molecule, and at the same time providing sufficiently numerous collisions to maintain approximately Boltzmann rotational equilibrium throughout the band, should always produce some degree of inversion in the lines near the longer-wave side of that band.

However, the farther toward the shorter-wave side one chooses for pumping, the more intense the pumping must be before inversion becomes appreciable. This generality is one of the bases of the transformer laser concept being explored in the present work.

Figure 11 shows the relation between $\left[Z_0 \right]_{80}$ and spectrum line wavenumber for the (0, 0) band of $N_2 \cdot (B - A)$, based on Σ values obtained during the calculation of Boltzmann distributions. As Herzberg's book shows, $\Sigma \approx kT/hcB$ for the levels of a simple rotator whenever T is large or B is small; but with these more complicated levels of the nitrogen molecule, analytic expressions for Σ are not very useful.

An approximation to the corresponding relation between $\left[Z_0 \right]_{80}$ and σ for the (1, 0) band of $N_2 \cdot (B - A)$ is indicated by the percentages at the bottom of Figure 7.

In summary, it appears that a repetitive pump-lase transformer cycle could be set up in any band of the nitrogen 1st Pos. system absorbing the pump light for which a strong population in the lower vibrational level could be "prepared", and maintained against population losses. In the next section the basic assumption that losses from $N_2 \cdot A$ will not be intolerable, as well as the question of the actual $N_2 \cdot A$ population density needed for useful transformer action, will be discussed.



5. EXCITED-STATE POPULATION LIMITS ON NITROGEN TRANSFORMER POWER

5.1 Population Needed For a Desired Power Density

At wavelengths near 1μ it requires about 5×10^{18} quanta to total an energy content of 1 joule. We define \mathcal{N} as the total number of molecules in a typical cm^3 of gas near the output end of the transformer medium which are resident in $\text{N}_2 \cdot \text{A}$ and $\text{N}_2 \cdot \text{B}$ throughout a power pulse. In section 10.4 of report GPL A-31-1 there is described the manner in which a fraction of such molecules will be carried repeatedly around a four stage pump-lase cycle, under conditions of very intense pumping flux and very intense lasing flux. From the appearance of Figure 23 in that report, and of Figure 10 in the present report, it is estimated that the fraction of \mathcal{N} which will be taken repeatedly around this cycle in the nitrogen case will be somewhere around 1%, and that the time for a molecule to traverse the cycle once will average about the time required for this molecule to suffer 3 classical kinetic theory collisions in the ambient vapor — under collision-limited transformer operation. If this vapor is either all N_2 , or partly N_2 and partly He, at \underline{p} atmospheres total pressure and 80°K , a given N_2 molecule will experience about $\underline{p} \times 1.2 \times 10^{10}$ coll/sec.

On the above bases, the number of metastable molecules required for the development of an energy of E joules/ cm^3 in a high flux region near the output end of the transformer medium, during a power pulse of \underline{t} sec, will be given by the following approximate expression:

$$\frac{n \times 10^{-2} \times pt \times 1.2 \times 10^{10}}{5 \times 10^{18} \times 3} = E$$

$$n = \frac{1.3 \times 10^{11} E}{pt} \quad \text{molecules in } N_2 \cdot A \text{ and } N_2 \cdot B \text{ per cm}^3.$$

One sample set of parameters, $E = 1$, $t = 10^{-3}$, $p = 1$, would require maintenance of about 10^{14} excited molecules/cm³ throughout the pulse.

Other situations can be estimated from the formula as desired. The pumping and lasing flux density requirements for yielding collision-limited conditions, such that the above equation would apply, will be discussed at a later time.

It might be useful for future reference to state the relation between n and E in a generalized fashion for pumping and lasing in a given wavelength region and at sufficient high fluxes to yield collision-limited conditions:

$$n \sim \left[\frac{(\text{Number of collisions per pump-lase cycle})}{(\text{Pulse length}) \cdot (\text{Molecular collision rate}) \cdot (\text{Fraction of } n \text{ traversing the cycle})} \right] \cdot E$$

Without continuing at present into the problems of "preparing" a very high concentration of $N_2 \cdot A$ molecules, beyond those points already mentioned in Section 2.3 let us now consider to what extent an initial concentration of $N_2 \cdot A$ can be maintained against losses, throughout a power pulse of appreciable length.

5.2 Fluorescence Losses From $N_2 \cdot A$

A molecule in any of the first 6 vibrational levels of electronic state $N_2 \cdot A$, and in any rotational sublevel of these which would normally have appreciable population at 80°K, can spontaneously radiate only to some level of $N_2 \cdot X$ of lesser energy. The spontaneous radiative lifetime of such an $N_2 \cdot A$ molecule has been the subject of much investigation, and the matter is not yet thoroughly settled. Values of τ_{spn} of some milliseconds have still been appearing in the literature quite recently, but Dr. N. P. Carleton of Harvard in a telephone communication to the present writer on October 28, 1965 said he thought it was probably about 12 seconds — although arguments still existed which could possibly make τ_{spn} come out as small as 1 second. Dr. E. C. Zipf, Jr., of the University of Pittsburgh, in a telephone communication to the writer on October 5, 1965 said that he thought this radiative lifetime was greater than about 15 sec and might be in the neighborhood of 21 sec. In any case, attempts at exact measurement have been beset with difficulties. $N_2 \cdot A$ molecules in higher vibrational levels than ($v = 6$) could also radiate, with relatively short lifetimes, to $N_2 \cdot B$. However, this would not remove them from the (B—A) pump-lase cycle here being considered.

5.3 Impurity Quenching of $N_2 \cdot A$

Of greater potential seriousness, and much greater complexity, is the problem of the lifetime against collision-quenching of the electronic

excitation for $N_2 \cdot A$ molecules under various circumstances. In the first place, at least in an electric discharge through low pressure nitrogen, it is found that extremely minute traces of oxygen impurity will severely quench $N_2 \cdot A$. Probably the discharge makes some NO molecules, which are known to have a very high cross section* for quenching $N_2 \cdot A$. Thus, Miller (1965) found that steady-state emission of the (A \rightarrow X) bands was very weak, and NO bands were very strong, in his discharge tube using reagent grade nitrogen with less than 4 ppm O_2 impurity — until he further purified the gas with Zr-Ti getter and carried out a very vigorous routine of pumping, baking, and long-term operating of the apparatus. Dr. Zipf (loc. cit.) suggests that impurities must probably be less than 1 part in 10^7 if the steady-state $N_2 \cdot A$ content in a discharge tube is not to suffer major depletion within about a millisecond after stopping the discharge.

However, no attempt has yet been made to create important concentrations of $N_2 \cdot A$ purely by optical pumping, without any discharge which could convert impurity oxygen into NO. Perhaps the purity requirements would not be so extreme in this case, although the ability of the unexcited oxygen molecule itself to quench $N_2 \cdot A$ has not yet been carefully measured. Safrany (1964) did show that excited nitrogen molecules in the state $N_2 \cdot A$ do not enter into a chemical reaction with O_2 to any major extent.

* Dr. Carleton said he has new quantitative data on this cross section almost ready for publication.

It is known^{*} that collisions with certain atomic impurities such as Hg, will also strongly quench $N_2 \cdot A$. However, added He would not be expected to cause any important degree of quenching.

5.4 Electronic-to-Vibrational Quenching of $N_2 \cdot A$

If we were dealing with strictly pure nitrogen gas, under non-discharge conditions at room temperature or below and at pressures of at least a few cm in apparatus of usual size, the most frequency collision partner of any $N_2 \cdot A$ molecule would be an $N_2 \cdot X$ molecule in ($v = 0$). If the $N_2 \cdot A$ was to be knocked down to $N_2 \cdot X$ from one of its lower vibrational states in such a collision, practically all of its electronic energy would have to be converted into vibrational energy of the two resulting $N_2 \cdot X$ molecules. There has been a continuing debate in the literature as to whether any evidence that this process has much probability can be deduced from discharge tube experiments.

Perhaps something can be inferred from a related field. There is much work which shows that vibration-to-translation energy transfer upon collision has very low probability whenever a Δv change much greater than unity within a given electronic state is required, or at least whenever the energy to be transferred is large compared to kT/hc . Applying the Franck-Condon principle to the potential curves shown in Figure 2, electronic-to-vibration quenching of $N_2 \cdot A$ ($v = 0$) in a two-body collision would usually require Δv to be about 13 for the original $N_2 \cdot X$ colliding partner. If the electronic-to-vibration process followed the same rules as vibration-to-translational relaxation, then

^{*} Janin (1946), for example.

quenching of $N_2 \cdot A$ by such collisions should be quite rare.

Considering electronic-to-vibration experiments, it has long been known that Na atoms in their first excited electronic level could have their fluorescence — under non-discharge conditions — very strongly quenched by collisions with $N_2 \cdot X$ molecules. If most of the Na electronic energy went into vibration it would produce $\Delta v = 7$ in the nitrogen molecule. This interpretation was generally accepted as early as in the Mitchell and Zemansky (1934) book, but attempts to prove it rigorously are still in process, as by Starr (1965). However, in the Pringsheim (1949) book several such atomic-to-molecular cases of electronic-to-vibrational energy transfer upon collision were considered in more detail. Evidence was brought forward that cases of such large Δv probably arose only because the potential energy curves were highly distorted during the collision interval, in such a way as to indicate incipient chemical reaction between the colliding partners. In collisions where there is no tendency toward chemical reaction, these large energy transfers should have very low probability. However, we cannot be sure that $N_2 \cdot A - N_2 \cdot X$ collisions do not have a considerable tendency to form a transient N_4^* molecule before re-separating — which is an incipient chemical reaction.

It appears that the probability of this type of loss from the $N_2 \cdot A$ population cannot be estimated directly from existing data. However, some additional indirect evidence will be mentioned in the next section which points to its probable unimportance under the assumed laser transformer conditions.

5.5 Metastable-Metastable Quenching of $N_2 \cdot A$

Another possible mechanism for loss of $N_2 \cdot A$ molecules during a power pulse would only become important at very high concentrations of excited molecules. But this is probably just the process which would place a ceiling on those practical values of η and E which could be attained in a transformer laser application.

This is a collision of one $N_2 \cdot A$ molecule with another $N_2 \cdot A$ molecule, or with an $N_2 \cdot B$ molecule, or with one in some other excited state. Electronic energy could then simply be transferred from one of the colliding partners to the other. An $N_2 \cdot A$ molecule would drop to one of the lower vibrational levels of $N_2 \cdot X$ such as ($v = 6$) — the probability distribution over these latter levels being governed by the Franck-Condon principle — and the colliding partner would use the released energy to climb to some much higher electronic state than it occupied initially. Other variations of this could occur, depending on the initial degree of excitation of the colliding molecules. Losses from $N_2 \cdot B$ could also occur in this way as well as losses from $N_2 \cdot A$, during a power pulse. Cases of such mostly electronic-to-electronic energy transfers are already known to display high probability in various molecular and atomic-molecular collisions. Pringsheim (1949) summarized much information of this type.

Apparently, the only experimental data on this mechanism have been gathered recently by Zipf (1964), under somewhat complicated discharge tube conditions. Earlier workers had probably not been dealing with large enough $N_2 \cdot A$ concentrations for the process to become observable. After establishing steady-state concentrations in his discharge volume, believed to be about $10^{11} N_2 \cdot A/cm^3$, or slightly higher, Zipf stopped the discharge and observed that the decay of the $N_2 \cdot A$ population density during the next few milliseconds of the afterglow period followed a second-order rate equation.* That is,

$$\frac{d[N_2 \cdot A]}{dt} = -k_2 \cdot [N_2 \cdot A]^2 \quad .$$

This was interpreted to mean that the $N_2 \cdot A$ molecules were disappearing as a result of $(N_2 \cdot A - N_2 \cdot A)$ collisions, whose probability of occurrence at any time would naturally be proportional to the square of the instantaneous $N_2 \cdot A$ population density.

* The predominance of this second-order decay would argue that first-order decay of $N_2 \cdot A$ by electronic-to-vibration collision transfer is negligible by comparison with the second-order process at $10^{11} N_2 \cdot A$ per cm^3 or more.

Such a loss mechanism, which rapidly increases in importance as the $N_2 \cdot A$ population density is made higher, could be expected to set a practical ceiling on achievable $N_2 \cdot A$ population density in many kinds of situations. Neither Dr. Zipf nor Dr. Carleton have been able so far to get above perhaps 10^{12} $N_2 \cdot A$ molecules/cm³ steady-state concentration, in the discharges in their apparatuses. *

Integration of the second-order rate equation immediately shows that the time for an $N_2 \cdot A$ population density to decay to one half its initial value $[N_2 \cdot A]_0$ is given by

$$\tau_{A-A} = \frac{1}{k_2 [N_2 \cdot A]_0}$$

Using Dr. Zipf's latest value for the second-order rate constant, $k_2 = 3 \times 10^{-11}$ cm³ · (molecules)⁻¹ · sec⁻¹, if one began a transformer laser power pulse with η molecules/cm³ in $N_2 \cdot A$ plus $N_2 \cdot B$, half of them would have disappeared by this mechanism after

$$\tau_{A-A} = \frac{10^{11}}{3 \times \eta} \text{ sec.}$$

* According to telephone communications previously noted.

The sample parameters used for illustration in Section 5.1 would lead to $\tau_{A-A} = 1/3$ millisecond. The needed $N_2 \cdot A$ concentration would have been largely lost during the power pulse interval for these assumed parameters, unless it was constantly being replenished by continuing the UV preparatory flash throughout the power pulse.

There is no experimental evidence as to whether k_2 , and consequently τ_{A-A} , vary with the temperature of the gas. Therefore, one cannot be sure whether the situation would be any better at 80 K than under Dr. Zipf's discharge conditions.

Another piece of evidence should be considered. Dunford, Milton, and Whalen (1964) have reported some phenomena in a discharge tube through a mixture of nitrogen and ammonia, known to contain considerable oxygen impurity, for which they suggest an interpretation that implies the initial presence of $4.5 \times 10^{14} N_2 \cdot A$ molecules/cm³, with these decaying after the end of the discharge with a half-life of 80 milliseconds. One immediately apparent way to reconcile this finding with the 1/3 ms half life just computed by extrapolating Zipf's results to the initial concentration range of $10^{14} N_2 \cdot A$ per cm³, would be to postulate some process in this very complicated discharge mixture which continued to feed fresh molecules into the $N_2 \cdot A$ long after the discharge ceased — which is certainly plausible. In any event, these circumstances seem too complicated to be employable in a laser transformer design.

* It should be noted that Zipf's experimental technique actually measures the product of k_2 times the partial τ_{spon} for the (0,6) band of the $N_2 \cdot (A-X)$ radiative transition. The above value of k_2 is then calculated from other measurements of the (0,6) band strength. The measurements used by Zipf, together with a ratio of the (0,6) lifetime to the total $N_2 \cdot A$ lifetime calculated from theoretical Franck-Condon factors, imply a value of the total $\tau_{\text{spon}} = 20$ sec for $N_2 \cdot A$. If subsequent work should ever return the total τ_{spon} to 1 sec. for $N_2 \cdot A$, as Dr. Carleton mentioned was conceivable, the above k_2 value should be increased by a factor of 20, and calculated values of τ_{A-A} would be decreased by a factor of 20.

5.6 Losses from $N_2 \cdot B$

If the ambient gas pressure could be raised to 10 atm, the required η would be reduced by a factor of 10, τ_{A-A} would be increased by a factor of 10, and the unfavorable result of the last section would be ameliorated — under the assumed conditions. If it should be undesirable to have so much $N_2 \cdot X$ present, practically all of the mixture could be He. Any kind of added entities which would increase the collision rate without other bad effects would improve the ratio of needed η to E.

However, it is uncertain how much total ambient pressure of any mixture could be employed without increasing the importance of losses from $N_2 \cdot B$. The one atmosphere assumed above might actually be too much. There are no adequate data available, for the reason that conditions have not been set up hitherto which could be expected to lead to large concentrations of $N_2 \cdot B$. Nitrogen molecules in $N_2 \cdot B$ have a lifetime of only about $10\mu\text{sec}$ against spontaneous radiation of the First Positive bands, thereby dropping to $N_2 \cdot A$. Only under the very high-flux cycling conditions postulated for the present transformer laser design would it be very practical to try to maintain a high concentration of $N_2 \cdot B$ over an appreciable volume for times of the order of a millisecond.

If the chosen pump-lase cycle is to involve only the (0, 0) First Positive band, then the trouble to anticipate from high ambient pressures could arise from a high probability that any kind of collision

would shift an $N_2 \cdot B(v = 0)$ molecule over into the $^3\Delta_u$ state — with unknown further fate. Of course, this problem would not be present if $^3\Delta_u$ actually lies considerably above $N_2 \cdot B$, instead of below as sketched in Figure 2. If the cycle involves major population densities in $(v = 4)$, or higher of $N_2 \cdot B$, then transfer to $^3\Delta_u$ as well as to states B' , a' , a , and w might cause major losses at high collision rates.

One might think that at high pressures all of these metastable states could simply be saturated, during the "preparation" period and the first few μsec of the power pulse, so that back-reactions would thereafter maintain a steady $N_2 \cdot B$ concentration. However, it could happen in such a case that the total metastable population would be so high that metastable-metastable collisions would soon be carrying too many molecules above the dissociation limits. Actual dissociation of the nitrogen molecules as a result of the optical pumping could not be tolerated to any very great extent, since the heat of recombination would deteriorate the optical quality of the medium.

Jeunehomme and Duncan (1964) measured the rate of fluorescent decay of the 1st Pos. bands in the afterglow from a discharge as a function of nitrogen pressure up to 6mm only. They observed a somewhat faster decay rate at the higher pressures. However, it is not certain that this was caused by losses from $N_2 \cdot B$, rather than by some phenomenon involving the higher levels excited by the discharge, which were possibly feeding $N_2 \cdot B$ during the observation period.

Noxon (1962) followed the decay of the 1st Pos. bands in the after-glow from a discharge at 1 atm nitrogen pressure. However, his results only sufficed to demonstrate that collisional removal of $N_2^+ B$ at 1 atm pressure could not be more than four times faster than radiative decay from this level, so they offer no information about the possibility of maintaining a large $N_2^+ B$ population into the millisecond time range.

6. CONCLUSIONS ON NITROGEN AS A TRANSFORMER MEDIUM WITH Nd PUMPING

A complete bibliography of research papers on properties of the nitrogen molecule would doubtless contain several thousand entries. Many more of these papers have been studied during this contract period than are referenced in this report. Yet despite all this work, information is still lacking on a considerable number of the parameters which would be involved in the design of an ultra high power transformer based on nitrogen gas, or nitrogen plus helium, pumped by Nd glass lasers. Quite intricate research would be needed to fill this gap.

Transformer action based on metastable $N_2^+ A$ molecules seems entirely possible, but sufficient data are not available today to give optimism that the transformer laser power density range of one or more joules/cm³ per pulse will be attainable with good optical quality of the output beam.

7. MONOMER POPULATION LIMITS ON CYANOGEN TRANSFORMER POWER

7.1 Population Needed for a Desired Power Density

Report GPL A-31-1 dealt chiefly with the possible use of diatomic cyanogen monomer molecules plus helium gas as a transformer medium with Nd glass laser pumping. Let us now apply to this medium the same type of population limit analysis which was just carried out for N_2 •A.

Again, the total density of those CN molecules which are to be resident in the upper and lower vibration states of a proposed pump-lase cycle throughout the power pulse will be called η . It was shown in the previous report that about 1% of this number of molecules/cm³ would probably be travelling around the cycle under very high flux conditions, and that the number of CN-He collisions needed per cycle for shifting rotational populations might be about four. At 210°K, the classical kinetic theory rate of He collisions against a given CN•X molecule would be about $p \times 1.4 \times 10^{10}$ per sec, when the partial pressure of helium was p atmospheres. This figure follows from using for CN the collision diameter $D_1 = 4.4 \times 10^{-8}$ cm from Evenson, Dunn, and Broida (1964), together with the He value of $D_2 = 2.18 \times 10^{-8}$ cm, in the usual formula*

$$\theta_{12} = 2 \left(\frac{D_1 + D_2}{2} \right)^2 n_2 \sqrt{\frac{2\pi R_M T (M_1 + M_2)}{M_1 M_2}} \text{ collisions/sec,}$$

* See, for example, Kennard (1938).

where n_2 is the number of helium molecules/cm³ in the gas, M_1 and M_2 are the molecular weights, T is the absolute temperature, and R_M is the gas constant per mole, 83.15×10^6 cm-dynes/degree.

In the same fashion as for $N_2 \cdot A$, these assumptions lead to the relation

$$\frac{n \times 10^{-2} \times p t \times 1.4 \times 10^{10}}{5 \times 10^{18} \times 4} = E$$

$$n = \frac{1.4 \times 10^{11} E}{p t} \text{ molecules/cm}^3.$$

The same sample set of parameters as used with nitrogen, $E = 1$, $t = 10^{-3}$, $p = 1$, would again require maintenance of a little over 10^{14} CN molecules/cm³ in the desired vibrational states throughout the power pulse, under collision-limited cycle conditions.

In the next sections the most important processes will be considered which might prevent maintenance of the necessary CN vibration state population density throughout the pulse, under various pressure, power density, and pulse length assumptions.

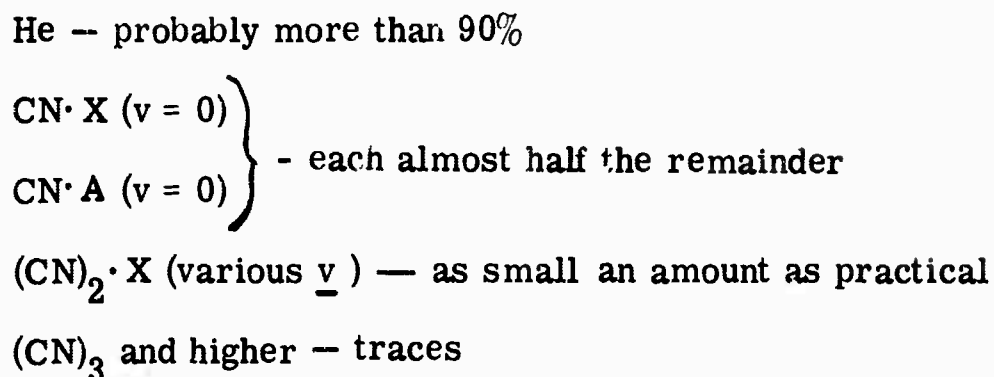
7.2 Types of Collision Processes Possible in the Cyanogen Medium

In the manner described in Report GPL A-31-1, the transformer medium at the beginning of a pulse sequence would consist of somewhat more than $n/2$ molecules/cm³ of (CN)₂ in p atm of helium gas, when it was desired to reach a maximum power pulse density of E joules/cm³.

The mixture would be irradiated with a preparatory pulse of light at about 2000Å wavelength, which would convert as large a fraction as possible of the (CN)₂ molecules into pairs of CN molecules. After at most a few μsec, the mixture would consist of largely He, CN·X, and (CN)₂·X molecules — plus perhaps a very few molecules of (CN)₃ and higher polymers which had already begun to form as a result of collisions between the new CN fragments and any remaining (CN)₂ molecules.

Let us assume that the power cycle will operate in the (0, 0) band of the CN·(A — X) system. Then a further flux in the preparatory pulse to put CN·X molecules into higher vibrational levels will not be necessary. All the CN·X will be taken as resident in ($v = 0$). In the first few μsec of the power pulse we might pump sufficiently hard in the (0, 0) band to convert about half the CN·X ($v = 0$) molecules into CN·A ($v = 0$) molecules.

The constitution of the mixture would then be:



Throughout the power pulse duration, these entities will be colliding with each other, and the concentration of the various higher polymers will be slightly increasing. Table 2 lists the major types of collision processes which are possible, in principle. For very few of these processes are the rates known quantitatively, but the most important ones can probably be identified with reasonable confidence.

Of the two-body processes, simple recombination is known to always proceed rather slowly, although there appear to be no quantitative data available for CN-CN. That is, two CN·X or two CN·A molecules, or a CN·X plus a CN·A, cannot make (CN)₂ in a two-body collision with much probability, because of the momentum conservation law. A third body is usually needed to carry away the heat of recombination as kinetic energy.

Colliding Molecules			Product Molecules			
	1	2	3	1	2	3
<u>TWO-BODY COLLISIONS:</u>						
	CN•X	HE		ROTATION-SHIFTING ONLY		
	"	CN•X		(CN) ₂		
	"	CN•A				
	"	CN•A		CN•X (v = 0)	CN•X (HIGH v)	
	"	(CN) ₂		(CN) ₃		
	"	(CN) ₂ ₃		(CN) ₄		
	CN•A	HE		ROTATION-SHIFTING; VERY LITTLE		
	"	CN•A		QUENCHING		
	"	"		CN•X	CN•A (HIGH v)	
	"	"		(CN) ₂		
	"	(CN) ₂		(CN) ₃		
	"	(CN) ₃		(CN) ₄		
	(CN) ₂	(CN) ₃		?		
	(CN) ₃	HE		?		
	(CN) ₃	(CN) ₃		?		
<u>THREE-BODY COLLISIONS:</u>						
	CN•X	HE	HE	ROTATION-SHIFTING ONLY		
	CN•A	"	"	CN•X	HE	HE
	CN•X	CN•X	"	(CN) ₂	"	
	"	CN•A	"	"	"	
	CN•A	"	"	"	"	
	CN•X	CN•X	CN•X	(CN) ₂	CN•X	
	"	"	"	(CN) ₃		
	"	"	CN•A	(CN) ₂	CN•X	
	"	"	"	(CN) ₃		
	"	"	"	CN•X	CN•X	CN•X
	"	CN•A	CN•A	(CN) ₂	CN•A	
	"	"	"	"	CN•X	
	"	"	"	(CN) ₃		
	"	"	"	CN•X	CN•X	CN•A
	"	"	"	CN•X	CN•X	CN•X
	CN•A	CN•A	CN•A	(CN) ₂	CN•A	
	"	"	"	"	CN•X	
	"	"	"	(CN) ₃		
	"	"	"	CN•X	CN•A	CN•A
	"	"	"	CN•X	CN•X	CN•A
	"	"	"	CN•X	CN•X	CN•X
	CN•X	CN•X	(CN) ₂	(CN) ₃	CN	
	"	"	"	(CN) ₄		
	ETC.					
	ETC.					
	ETC.					

Table 2. Collision Processes in the Cyanogen Medium.

The two-body process having the highest probability per collision will probably be the polymerization to $(\text{CN})_3$ which occurs when $\text{CN}\cdot\text{X}$ or $\text{CN}\cdot\text{A}$ hits one of the remaining dimers $(\text{CN})_2$. The only way apparent so far to keep this from leading to excessive loss of CN is to make the preparatory UV flash so powerful that it will dissociate almost all the original dimer, leaving very few $(\text{CN})_2$ molecules present at the start of the power pulse.* This arrangement was considered in the previous report, and the extent to which it can probably be accomplished will not be discussed further here.

Any $\text{CN}\cdot\text{X}$ - $\text{CN}\cdot\text{A}$ collisions which electronically quenched $\text{CN}\cdot\text{A}$, a process of appreciable probability because incipient chemical combination might perturb the potential curves, as discussed in the nitrogen case, would slightly reduce the transformer efficiency by throwing away one Nd pump quantum for each such quenching. However, this would not actually constitute a loss of available CN molecules during the power pulse.

Although in many circumstances three-body collisions are usually assumed to occur with only about one thousandth the frequency of two-body collisions, one of the three-body processes listed actually seems likely to prove the determining factor in the use of CN as a transformer medium.

Of course, the most prevalent three-body collision in the mixture will be two He against a CN, either $\text{CN}\cdot\text{X}$ or $\text{CN}\cdot\text{A}$. However, these should not have much deleterious effect. The important case is the next most

*However, it appears possible that further quantitative analysis of the collision process rates might considerably reduce the stringency of this requirement.

probable one — two CN's against one He — which is a somewhat powerful process for polymerizing the CN's to $(\text{CN})_2$. The effect of the He is mostly not a chemical one; it merely provides a second body emerging from the collision, so that the momentum conservation law will now permit conversion of potential energy into translation, with the result of stabilizing the dimer before it can re-dissociate. In the next section such collisions will be considered in some detail.

7.3 Three-Body Recombination of CN in Helium

This process will follow a third-order rate equation:

$$\frac{d[\text{CN}]}{dt} = -k_3 [\text{CN}]^2 [\text{He}]$$

where the brackets indicate respective instantaneous concentrations in molecules or atoms per cm^3 . Since during any given pulse the helium concentration will remain constant, the CN concentration will follow a pseudo second-order rate equation

$$\frac{d[\text{CN}]}{dt} = -k'_2 [\text{CN}]^2$$

where k'_2 is proportional to the helium concentration used in the mixture,

$$k'_2 = k_3 \cdot [\text{He}]$$

As in the nitrogen case, the CN concentration will decrease to half its initial value in a time

$$\tau_{\text{CN-CN-He}} = \frac{1}{k'_2 \cdot [\text{CN}]_0} = \frac{1}{k_3 \cdot [\text{He}] \cdot [\text{CN}]_0}$$

The value of k_3 for three-body recombination of CN has not been measured with He as the third body, but Basco, Nicholas, Norrish, and Vickers (1963) obtained $k_3 \approx 1.7 \times 10^{16} \text{ (milliliters)}^2 \text{ (moles)}^{-2} \text{ sec}^{-1}$ at room temperature with N_2 as the third body. The view that the chemical nature of the third body is not seriously involved in this process might be taken to receive some support from the fact that Smith (1962) found a value of k_3 for the three-body recombination of iodine atoms with He as the third body only a factor of 10 smaller than this one. If we assume that the use of He with cyanogen would lead to about the same k_3 as with N_2 , we can change the units and obtain

$$\begin{aligned} k_3 &\approx 1.7 \times 10^{16} \frac{(\text{milliliters})^2}{(\text{moles})^2 \cdot \text{sec}} \times 1 \left(\frac{\text{cm}^3}{\text{milliliter}} \right)^2 \times \left(\frac{1}{6 \times 10^{23}} \right)^2 \left(\frac{\text{moles}}{\text{molecules}} \right)^2 \\ &\approx 4.7 \times 10^{-32} \text{ (molecules/cm}^3\text{)}^{-2} \cdot \text{sec}^{-1} \end{aligned}$$

These are the appropriate units for the third-order rate equation in the form stated at the beginning of this section. With the sample parameters assumed in Section 7.1,

$$\tau_{\text{CN-CN-He}} \approx \frac{1}{4.7 \times 10^{-32} \cdot \left(\frac{273}{210}\right) \cdot \left(\frac{6 \times 10^{23}}{2.24 \times 10^4}\right) \cdot 1.4 \times 10^{14}}$$

$$\approx 4.4 \times 10^{-3} \text{ sec,}$$

on the further assumption that k_3 does not vary with temperature.

If we assume He to be a factor of up to 10 less conducive to three-body recombination of CN than N_2 , then the margin of safety would be still greater, and initial concentrations rather higher than $10^{14}/\text{cm}^3$ could be considered.

Combining the equation relating η and E with the formula which defines the above τ gives the following result:

$$\frac{\tau_{\text{CN-CN-He}}}{t} \sim \frac{1}{E}.$$

This means that the ratio of half life against three-body recombination to pulse length, is independent of both helium pressure and pulse length. The degree of loss of CN molecules during the power pulse is proportional only to the energy density employed. Therefore, changing the pulse length or the helium pressure will not lift the practical power density ceiling set by this process.

8. CONCLUSIONS ON CYANOGEN AS A MEDIUM WITH Nd PUMPING

If all the assumptions involved in this calculation turned out eventually to be justified, it would seem with a 1ms pulse length that maximum output energy densities of the general order of $E = 1 \text{ joule/cm}^3$ or somewhat greater might be attainable — in so far as the limit is set by the processes considered so far.

However, many more considerations remain to be explored before monomer cyanogen plus helium could be definitely recommended as a practical transformer medium in this power density range. One strong advantage which CN will have over N_2 is in addition to better resistance against decay of the prepared entities, is its far larger absorption coefficient for the UV wavelength needed in the preparatory flash. This makes it greatly easier to obtain a UV source suitable for preparing a desired population density.

9. ADDITIONAL MEDIA CONSIDERED DURING THE REPORT PERIOD

9.1 The Se_2 Molecule

One of the possible media listed but not discussed in report GPL A-31-1 was a vapor of diatomic selenium molecules. During the present period the literature on properties of selenium vapor has been surveyed to some extent.

At any practical temperature selenium vapor is always found to consist of a mixture of diatomic and various polyatomic molecules in equilibrium with each other. For any temperature at which an adequate concentration of Se_2 is present, there is also a large concentration of Se_6 .

Such a large molecule as Se_6 will always have a multitude of fundamental, harmonic, and combination vibrational frequencies. In many experimental situations such polyatomic molecules are well known to cause severe quenching of energy stored in excited states of other molecules, by collision transfer of the stored energy into one of the vibrational modes of the large molecule. This would seem to make it extremely difficult to operate a transformer cycle on the Se_2 (A - X) transition without excessive degeneration of the absorbed pumped light energy into heat in the vapor.

In view of the apparent impracticability of obtaining reasonably pure Se_2 vapor, study of this molecule was not carried further.

9.2 The I_2 Molecule

The possibilities for employing iodine vapor as the transformer medium with Nd glass laser pumping were also considered more carefully than before. Here, the difficulty is that the Nd wavelength falls in a part of the $I_2 \cdot (A-X)$ band system which corresponds to absorption from quite high vibrational levels in $I_2 \cdot X$.

The vibrational spacing in I_2 is sufficiently small that vibration-to-translation energy transfer upon collision is very prevalent. Therefore, the transformer cycle would have to operate at fairly close to Boltzmann vibrational population distributions at all times. Under these circumstances, the only way to maintain an adequate population in the levels of $I_2 \cdot X$ from which the Nd light quanta could be absorbed would be to operate at quite a high vapor temperature.

However, this would place large populations in correspondingly high vibrational levels of $I_2 \cdot A$, and it is well known that collisions which dissociate molecules in these levels of $I_2 \cdot A$ have a very high probability. No practical way is apparent for using I_2 as the desired medium without an excessive amount of transformation of the pump light energy into eventual heat in the vapor, through the mechanism of dissociation of the $I_2 \cdot A$ molecules in high temperature collisions.

9.3 The CO Molecule and Others

As listed in report GPL A-31-1, the transition $\text{CO} \cdot (a \rightarrow a')$ appears to be quite analogous to the $\text{N}_2 \cdot (A \rightarrow B)$ transition in its possibilities for transformer use with Nd glass pumping. Its properties have not yet been thoroughly studied under this contract.

Harteck, Reeves, and Thompson (1964) have shown that metastable $\text{CO} \cdot a$ molecules display a high probability for chemical reaction upon collision with another carbon monoxide molecule, presumably in the state $\text{CO} \cdot X$, to form CO_2 and C. Very likely this mode of decay of $\text{CO} \cdot a$ would predominate in a heavily pumped medium and would set the limit on possible power output density. However, quantitative rate data are not yet available either for this reaction or for other CO collision processes which would doubtless be involved in a transformer application.

Although there is little solid evidence, there is no reason apparent today to expect better results from the CO molecule than from N_2 .

Those categories of possible diatomic molecules listed in report GPL A-31-1 as "not yet studied", were also explored to a considerable extent during this period, including such molecules as InCl^* , but without discovering any additional promising materials.

Polyatomic molecules have not yet been studied further. In view of their propensities for quenching, it was not thought profitable to explore them so long as a suitable diatomic molecule was available for the Nd laser transformer medium. At the present time, the best diatomic molecule seems to be Cs_2 , which will be mentioned briefly in the following section and analyzed carefully during the coming report period.

9.4 The Cs_2 Molecule

As discussed in report GPL A-31-1, the Cs_2 (A — X) transition will absorb Nd glass laser light quite strongly. The writer of this section has now had the opportunity of looking at the still unanalyzed spectrographic plates of this band recently taken in absorption under very high resolution at the Argonne National Laboratory by Prof. P. Kusch's group, of Columbia University. To the eye it appears that this band system has a quite simple structure, typical of a single electronic transition in a diatomic molecule — rather than consisting of overlapping allowed transitions as had been feared earlier.

On the problem of second-quantum absorption discussed in the previous report, GPL Division is now setting up apparatus for obtaining experimental data. The first preliminary tests are described in Section 10.

10. EXPERIMENTS ON THE SPECTRUM OF Cs₂

A preliminary experiment has been started to see if Cs₂ molecules which have already absorbed one quantum of Nd light to reach the excited state Cs₂ · A, can then absorb a second quantum of Nd light with possibly wasteful effects.

The first phase of the work has been concerned with the containment of the Cs vapor and the observation of the absorption bands corresponding to the (Cs₂ · A ← Cs₂ · X) and (Cs₂ · B ← Cs₂ · X) transitions. The observation of the absorption is a test for the existence of the Cs₂ molecules in the vapor.

Several Cs absorption cells have been prepared, by distillation of Cs metal into chemically cleaned and baked out, evacuated pyrex spheres. The spheres were blown to about 1" in diameter.

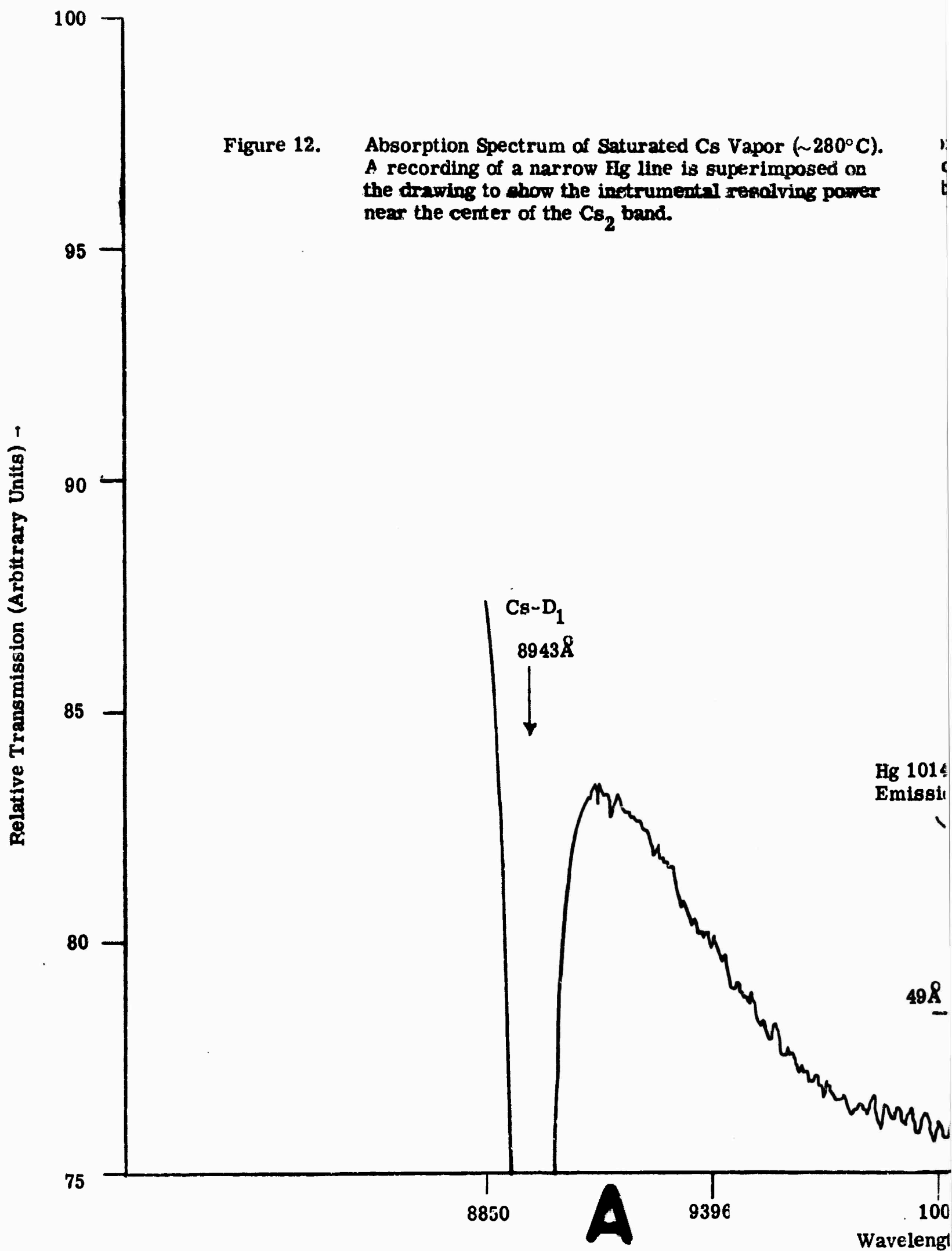
The absorption spectrum of the Cs cell was carefully measured at several temperatures between room temperature and 234°C. A dual beam absorption photometer arrangement was set up with a Leiss monochromator and absorption cell in an oven in one arm. A tungsten lamp served as the light source. The light levels in the reference and absorption arms of the light bridge were sensed with PbS photo-detectors, whose outputs were subtracted in a difference circuit. The quantity recorded as the output was the value of a resistor in one arm of the bridge that was adjusted to yield a null

in the output of the difference circuit as the wavelength examined was shifted with the monochromator. The relative transmission through the Cs vapor was obtained by normalizing the recorded output in such a way as to eliminate differences other than those caused by Cs vapor in the absorption of the two paths transversed by the reference beam and the transmitted beam. This was done by dividing the output obtained with a Cs-filled cell by the output obtained with a similar cell at the same temperature but with no Cs vapor in it.

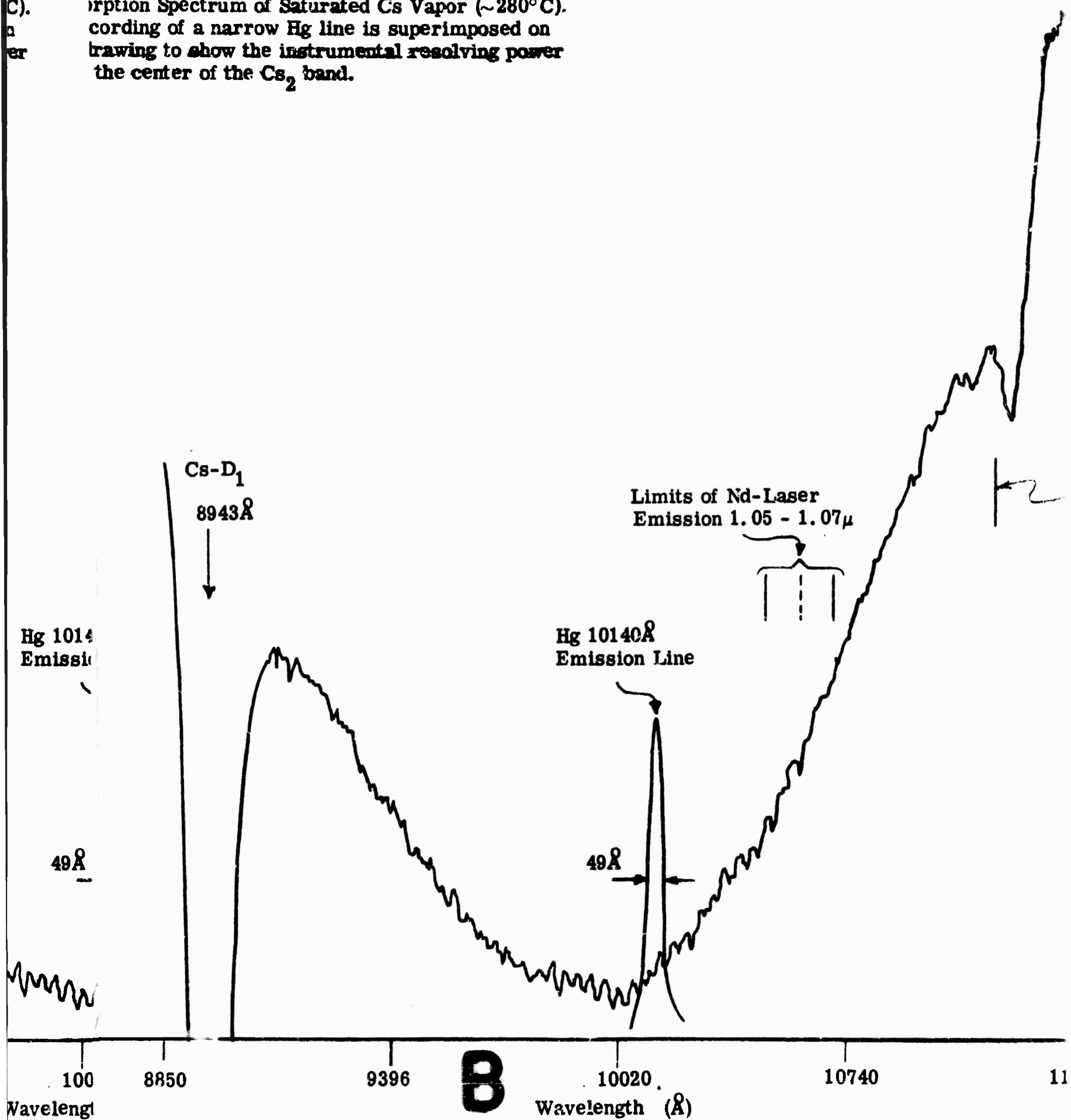
The transmission of the Cs vapor is shown as a function of the wavelength in Figure 12. A prominent feature is the Cs D_1 - line at 8943\AA arising from transitions between the $6^2S_{\frac{1}{2}}$ ground state and the $6^2P_{\frac{1}{2}}$ excited state of the Cs atom. The decrease in transmission beginning at the D_1 - line and extending to about $11,300\text{\AA}$, is in the region of the $(\text{Cs}_2 \cdot \text{A} - \text{Cs}_2 \cdot \text{X})$ group as reported by Finkelburg and Hahn (1938) and Loonis and Kusch (1934). The prominent structure found between $11,300\text{\AA}$ and $12,500\text{\AA}$ is in a region of the spectrum not previously reported. From the tests made to date this structure seems to arise from absorption by the vapor in the cell.

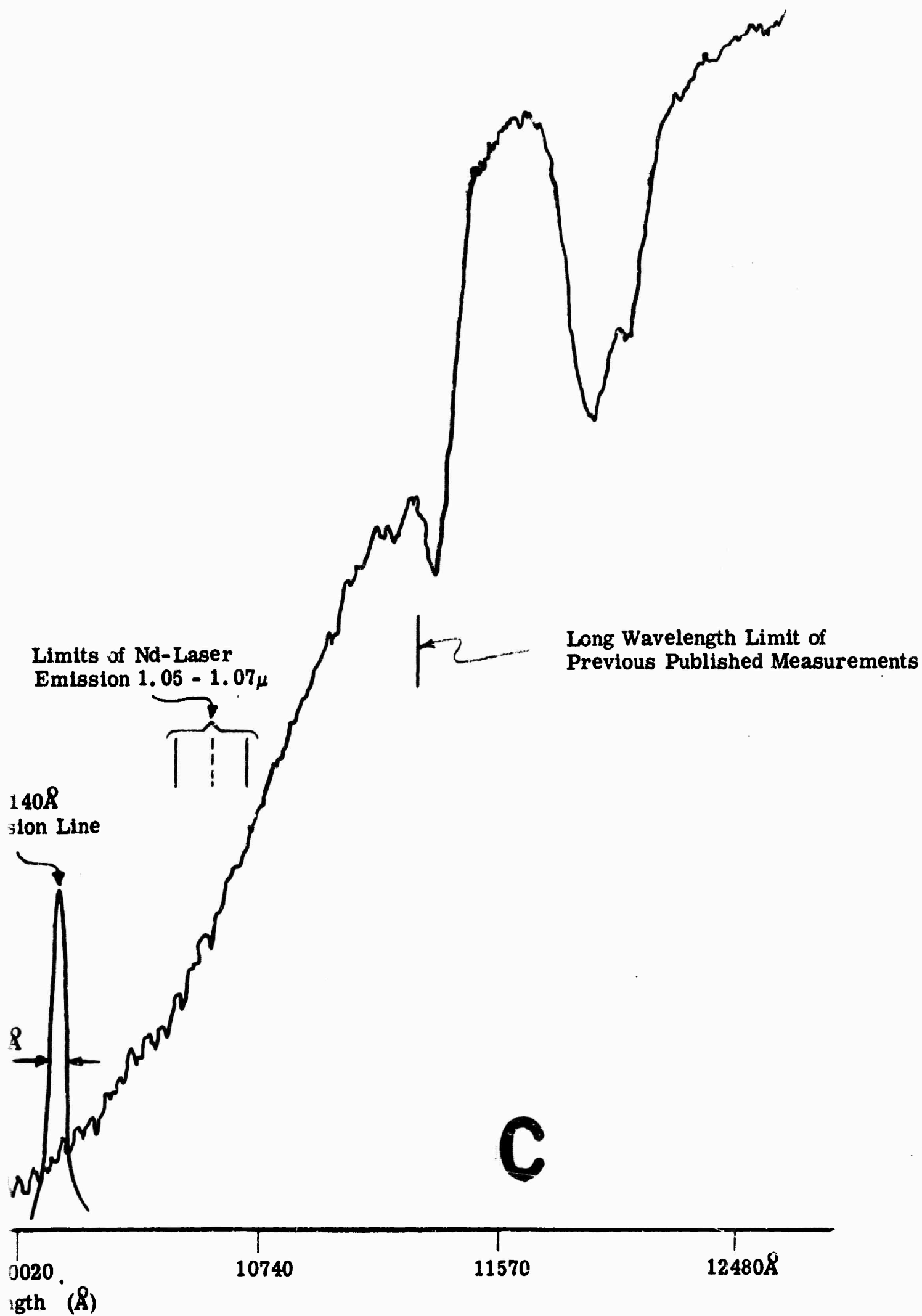
In this first experiment, the containment of Cs at elevated temperatures has been demonstrated and the existence of Cs_2 molecules in the Cs absorption cell has been observed. In the next experiments, absorption of the Nd-laser light will be investigated and the search made for the consequences of second quantum absorption by Nd-laser light.

Figure 12. Absorption Spectrum of Saturated Cs Vapor ($\sim 280^\circ\text{C}$).
A recording of a narrow Hg line is superimposed on the drawing to show the instrumental resolving power near the center of the Cs_2 band.



C). Absorption Spectrum of Saturated Cs Vapor ($\sim 280^\circ\text{C}$).
 Recording of a narrow Hg line is superimposed on
 drawing to show the instrumental resolving power
 the center of the Cs_2 band.





11. SPATIAL FLUX ANALYSIS

The spatial variation of the pump and laser fluxes within the volume of the active material is being studied. For describing the pump-lase cycle, an equivalent four-level system has been postulated in which the population densities, transition probabilities and collision rates represent suitably weighted averages taken over the multiplicity of possible levels of the actual system. The mechanism for population transfer, the corresponding level pairs, and the number density transfer rate for each portion of the pump-lase cycle are listed in Table 3.

TABLE 3
Pump-Lase Cycle, Equivalent Four-Level System

<u>Mechanism for Population Transfer</u>	<u>Level Pair</u>	<u>Number Density Transfer Rate</u>
Pump Flux	1 → 2	$\sigma_{12} P (N_1 - g_{12} N_2) = R_{12}$
Collisions	2 → 3	$k_{23} (N_2 - g_{23} N_3) = R_{23}$
Laser Flux	3 → 4	$\sigma_{34} L (N_3 - g_{34} N_4) = R_{34}$
Collisions	4 → 1	$k_{43} (N_4 - g_{41} N_1) = R_{41}$

In writing the expressions for the number density transfer rates R_{12} , R_{23} , R_{34} , and R_{41} the following assumptions were made:

1. The transfer rate from the equivalent level i to the equivalent level j will become zero when the averaged population density ratio $N_i/N_j = g_{ij}$, a weighting factor to be determined from the corresponding situation for the actual system..
2. The transfer rate caused by the pump (laser) flux is proportional to the pump (laser) photon flux intensity $P(L)$, to the weighted number density difference, $N_1 - g_{12}N_2$, $(N_3 - g_{34}N_4)$, and to an equivalent cross section σ_{12} (σ_{34}) for absorption (stimulated emission) of a pump (laser) photon.
3. The transfer rates produced by collisions are proportional respectively to the transition rates k_{23} and k_{43} and the weighted number density differences $N_2 - g_{23}N_3$ and $N_4 - g_{41}N_1$.

Within a given volume element of the gas, after illumination for a time sufficient to reach an equilibrium state and at such high pump and laser flux intensities that population changes caused by spontaneous emission and other losses become negligible, the number density transfer rates will be equal and constant in time. The rate equations for the equivalent four level system are then equivalent to the three conditions

$$R_{12} = R_{23} = R_{34} = R_{41}, \quad (1)$$

with the R_{ij} as defined in Table 3. The fourth condition is obtained from the assumption that within the given volume element the total number density N is constant in time, i. e., that

$$N_1 + N_2 + N_3 + N_4 = N. \quad (2)$$

Solution of these equations for the number density transfer rate R around the cycle, where

$R = R_{12} = R_{23}$, etc., gives

$$R = R_m \left[1 + (I_L/L) + (I_P/P) \right]^{-1} \quad (3)$$

where

$$R_m = N(1 - g_{12}g_{23}g_{34}g_{41})/\tau_c,$$

$$\tau_c = (A_{23}/k_{23}) + (A_{41}/k_{41}),$$

$$I_L = A_{34}/(\sigma_{34}\tau_c),$$

$$I_P = A_{12}/(\sigma_{12}\tau_c),$$

$$A_{12} = 1 + g_{41} + g_{34}g_{41} + g_{23}g_{34}g_{41},$$

$$A_{23} = 1 + g_{12} + g_{12}g_{41} + g_{12}g_{34}g_{41},$$

$$A_{34} = 1 + g_{23} + g_{12}g_{23} + g_{12}g_{23}g_{41}, \text{ and}$$

$$A_{41} = 1 + g_{34} + g_{23}g_{34} + g_{12}g_{23}g_{34}.$$

In the above, the parameter R_m is the limit approached by the absorption (or production) rate per unit volume of pump (laser) photons when both the pump and laser flux intensities become very large. The parameter I_P (or I_L) measures the pump (or laser) photon flux intensity at which the probability rate for an absorptive (or stimulated) transition becomes comparable with the effective collision induced transition rate, $1/\tau_c$ of the active molecule.

The spatial variation of the laser and pump flux intensities will be determined under the further condition that the total number density N is also uniform throughout the volume of active material. We can then equate the production rate R per unit volume of laser photons to the divergence of a vector \vec{L} whose direction is that in which the laser flux is propagating and whose magnitude is the laser photon flux intensity L , i. e.,

$$\nabla \cdot \vec{L} = R, \quad (4)$$

with R given by equation (3). Under the previous assumption that losses from spontaneous emission and other sources can be neglected the requirement for conservation of photons gives a second partial differential equation, namely,

$$\nabla \cdot (\vec{L} + \vec{P}) = 0, \quad (5)$$

where \vec{P} is the corresponding vector representation for the pump photon flux intensity.

In principle, solutions for equations (4) and (5) can be obtained once the incident laser and pump flux intensities are prescribed along the corresponding boundaries of the cell containing the active material. At present, an analytical solution has been obtained only by supposing incident laser and pump fluxes that have particular, and non-uniform, distributions over the input surfaces of the cell. It is considered, however, that this solution will prove to be a valuable guide toward specifying those incident laser and pump distributions which lead to an essentially uniform distribution for the laser output flux intensity.

For this preliminary case, the directions of \vec{L} and \vec{P} are assumed respectively parallel to the x and y axes of a rectangular coordinate system and both flux intensities are taken as uniform in the z direction. The solutions for L and P can be represented in terms of the quasi-exponential function $F(u)$ defined by the transcendental equation,

$$F/F_0 + A \log (F/F_0) = Bu + 1, \quad (6)$$

where $F_0 \equiv F(0)$ and u is a generalized variable. If the absolute value of the logarithmic term is large compared with $|F - F_0|/F_0$, the function $F(u)$ approximates a rising ($B > 0$) or falling ($B < 0$) exponential, whereas it is nearly linear in u when the logarithmic term is small. In particular, it is found that

- (a) $u = x - Cy$, where $C = L_o/P_o$, the ratio of the incident laser and pump flux intensities along the bounding line $x = 0 = y$,
- (b) $P(x, y) = F(x - Cy)$, and
- (c) $L(x, y) = CF(x - Cy) = CP(x, y)$.

The parameters A and B are given by

$$A = (I_L/L_o) + (I_P/P_o), \text{ and}$$

$$B = R_m/L_o.$$

In order for this solution to exist the trigger and pump lasers must be arranged to provide incident flux distributions, $L(0, y) = CF(-Cy)$, and $P(x, 0) = F(x)$, along the corresponding bounding planes $x = 0$ and $y = 0$.

The above solution is being used as a guide for analyzing the case in which pump flux is incident in opposite directions on two bounding planes, $y = 0$ and $y = y_1$, where y_1 is the width of the cell. Solutions of equations (4) and (5) in cylindrical coordinates are also being investigated.

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<p>Most of the analysis in this period has dealt with use of metastable nitrogen molecules as the active medium for a transformer laser to be pumped by a battery of Nd glass auxiliary lasers. It was concluded that such a medium would be operable, but that adequate data are not at hand to produce optimism on reaching maximum output pulse energy densities in the nitrogen greater than the region of one joule/cm³, with satisfactory maintenance of optical beam quality.</p> <p>An extension of previous analysis on a similar use of CN molecules indicates that this medium might be expected to yield satisfactory outputs around one joule/cm³ or somewhat greater.</p> <p>From the meager information available today, it appears that diatomic cesium molecules might possibly surpass CN and constitute the best medium for transformer action with Nd glass laser pumping.</p> <p>An experimental attack on some of the many remaining unknowns regarding Cs₂ is now underway, and first preliminary tests are reported.</p> <p>A beginning has been made toward mathematical spatial analysis of high power flux patterns to be expected within a heavily pumped transformer medium.</p>			

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